CANMET

Canada Centre for Mineral and Energy Technology

Centre canadien de la technologie des minéraux et de l'énergie

Energy Research Laboratories

Laboratoires de recherche sur l'énergie

Energy, Mines and Resources Canada

Énergie, Mines et Ressources Canada

Canada

THE ENERGY OF OUR RESOURCES • THE POWER OF OUR IDEAS

L'ENERGIE DE NOS RESSOURCES • NOTRE FORCE CREATRICE

9-92-77

CLASSIFICATION: NHRC, NOVA , Husky and Subsidiaries
NHRC REPORT #00576

HEAVY OIL BIOREACTOR

November, 1991

Author:

Mike McD. Francis
Les Stehmeier

Reviewed by:

Rolf Saetre
Tom Jack

DEPARTMENT: Biosciences
PROJECT NO: 5120
PREPARED FOR: Husky Oil Operations, Ltd., Calgary, and CANMET, EMR, Ottawa.
KEYWORDS: Bioreactor, sludge, oil degradation, peat, Oclansorb, leachate, analysis, absorbent, recycle, toxicity, Biosorb, Hazorb, Fuller's earth, MICROTOX.

This report contains the valuable proprietary and confidential information of the NOVA HUSKY Research Corporation and may not be used, disclosed or reproduced without permission in writing from NOVA HUSKY Research Corporation.

© 1992 NOVA HUSKY RESEARCH CORPORATION

DISTRIBUTION LIST

	Copies
Energy, Mines & Resources Canada:	5
Husky Oil Ltd.:	
Ralph Alm	1
Bert Faber	1
Darryl Howell	1
Marvin Kryska	1
Kong Ng	1
NOVA HUSKY Research Corporation:	
Mike Francis	1
Tom Jack	1
Rolf Saetre	1
Les Stehmeier	1
NOVA Corporation of Alberta:	
Tek Chin	1
Klaus Exner	1
Al Fedkenheur	1
Bob Martin	1
Phil Mason	1
Doug Taylor	1
NHRC Library	1
NOVA Library	1
Files	1
TOTAL NUMBER OF COPIES	23

© 1991 NOVA HUSKY RESEARCH CORPORATION

TABLE OF CONTENTS

Page #

EXECUTIVE SUMMARY iv

1.0 OBJECTIVE 1

2.0 INTRODUCTION 1

3.0 MATERIALS AND METHODS 1

3.1 The Bioreactor and Lysimeter Columns 1
3.2 Microbial Analyses 2
3.3 Water Analyses 2
3.4 Analysis of Extracted Oil 3
3.5 Flammability Testing of Bioreactor Matrix 4

4.0 RESULTS 4

4.1 The Bioreactor 4
4.1.1 Microbial Numbers in the Bioreactor 4
4.1.2 Water Analysis of the Bioreactor 4
4.1.3 Oil Contents of the Bioreactor 5
4.1.4 Characteristics of the Bioreactor Contents 5

4.2 Lysimeter Columns 6
4.2.1 Physical Appearance of the Lysimeter Columns 6
4.2.2 Microbial Numbers in Lysimeter Columns 6
4.2.3 Oil Contents of Lysimeter Columns 7

5.0 DISCUSSION 8

5.1 The Bioreactor 8
5.1.1 Microbial Numbers in Bioreactor 8
5.1.2 Oil Content of the Bioreactor 8
5.1.3 Disposal of Bioreactor Contents 8

5.2 Lysimeter Columns 11
5.2.1 Physical Appearance of Lysimeter Columns 11
5.2.2 Microbial Numbers and Oil Degradation in Lysimeter Columns 11
5.2.3 Evaluation of Recycled Oclansorb and Other Matrices for Oil Degradation 13

6.0 CONCLUSIONS 12

7.0 REFERENCES 14

8.0 TABLES 17

9.0 FIGURES 28

APPENDICES (1 TO 8)

© 1991 NOVA HUSKY RESEARCH CORPORATION

1.0 EXECUTIVE SUMMARY

A bioreactor for degradation of heavy oil sludges based on absorption of the sludge onto a matrix of Oclansorb, a heat treated peat product, was in operation at Husky Oil's Lloydminster asphalt refinery for 21 months. In spite of two unexplained losses of microbial numbers in the bioreactor, oil degradation levels of 46% for heavy oil from an API Separator sludge and 76% for a lighter oil fraction retained on a diatomaceous earth filter aid were obtained. The residual hydrocarbon in the bioreactor consisted of mainly asphaltenic material. The viable oil degrading microorganisms in the bioreactor were capable of growing on complex molecules containing up to 5 fused rings. No asphaltene degraders were enumerated and this correlated with an increase in the proportion of asphaltenes in the residual hydrocarbon in the bioreactor.

The leachate water from the bioreactor did not contain hydrocarbons, heavy metals or PAH's. It can be disposed of by methods normally used at the refinery or by deep well injection.

The matrix from the bioreactor can be reused at least once. Final disposal may be in a landfarm, or in a landfill. Based on a study of oil degradation in lysimeter columns, loading ratios of 1.7:1 - 1.8:1 (oil/Oclansorb) are possible. Other absorptive matrices suitable for use in the bioreactor include Biosorb, a heat treated peat produced in Alberta. Hazorb, an absorbent matrix made from expanded silicates was not suitable for use since it readily released adsorbed oil. Fullers' earth, a chemical absorbent made of aluminum and magnesium silicates, is probably too expensive relative to the peat products to merit serious consideration and showed plugging problems in lab trials. Biosorb is the cheapest absorbent, currently selling at nearly half the price of Oclansorb.

A bioreactor operation which landfills the spent reactor matrix after one reuse is an economically competitive disposal technique for low volume, high oil content waste streams.

© 1991 NOVA HUSKY RESEARCH CORPORATION

SOMMAIRE

Pendant 21 mois 46% de l'huile pesante et 76% de l'huile légère ont été dégradés dans un réacteur installé pour la biodégradation de l'huile a la raffinerie de Husky Oil Operations à Lloydminster, AB. L'huile était absorbée par un produit de la tourbe chauffée, nommée Oclansorb. Les hydrocharbons residuels dans le réacteur étaient des materiaux asphalteniques.

Les microbes dans le réacteur peuvent dégrader les molecules polynucleaires contennant jusqu'à cinq anneaux aromatiques. Il n'avait pas des organismes qui peuvent dégrader les materiaux asphalteniques.

L'eau dans le reacteur ne contennait pas de l'huile, des metaux pesants ou des molecules polynucleaires. Sa disposition n'est pas une problème.

On peut recharger la matrice du réacteur avec plus de l'huile au moins un fois. Puis, finalement, la matrice peut être amenee dans un landfarm ou dans un landfill. On peut la utiliser comme un additif pour ameliorer les sols sableus.

C'est possible a charger le réacteur jusqu'a 1.8:1 (huile/Oclansorb). Une autre matrice pour le reacteur est BIOSORB, une autre tourbe chauffee qui est vendue en ALberta.

Un réacteur qui est rechargé au moins un fois fait un façon économique pour disposer les déchets non volumineux contennants un niveau haut de l'huile.

© 1991 NOVA HUSKY RESEARCH CORPORATION

1.0 OBJECTIVES

- To determine the feasibility of using a bioreactor for microbial degradation of slop oils and sludges from a heavy oil refinery.
- To study, through the use of lysimeters, how different types of absorbents would function in a bioreactor.
- To discover if Oclansorb used in the bioreactor can be reused and the effects of loading higher oil concentrations on the matrix.
- To explore disposal options for the spent matrix from the bioreactor.

2.0 INTRODUCTION

Bench scale bioreactors in the laboratory at NHRC have established biodegradation of conventional and heavy oil sludges (1). A demonstration bioreactor at Lloydminster established heavy oil degradation in the field (2). After the Lloydminster bioreactor established enhanced biodegradation of slop oil, its continued operation was performed to determine the end point of degradation. Additional experiments conducted at NHRC investigated the maximum loading rates possible in the bioreactor, the reuse of the Oclansorb matrix and the use of different matrices for oil absorption in the bioreactor. This report is the result of that study.

3.0 MATERIALS AND METHODS

3.1 The Bioreactor and Lysimeter Columns

The bioreactor was constructed at Husky Oil's Lloydminster refinery (2). It was constructed in two sections (Figure 1). One section contained API separator sludge absorbed to Oclansorb and the other contained Oclansorb mixed with filter press aid (oil-contaminated diatomaceous earth from a filter press trial used to break slop oil emulsions generated from the desalter operation in the asphalt refinery).

Lysimeter experiments were conducted at NHRC. The experiment on maximum loading was conducted by mixing API separator sludge with Oclansorb in weight to weight ratios of 1:1, 2:1, 3:1 and 4:1 in lysimeter columns (65 cm x 6.5 cm I.D., Figure 2). API separator sludge was mixed with used matrix from the Lloydminster bioreactor in a ratio of 1:1 and placed in a lysimeter column to determine if Oclansorb matrix could be reused. Alternative matrices studied were Biosorb, an Alberta heat-treated peat; Hazorb, an absorbent based on expanded silicates, and Fuller's Earth, an absorbent consisting of aluminum and magnesium silicates. API separator sludge was mixed with Biosorb in 1:1 and 4:1 ratios

© 1991 NOVA HUSKY RESEARCH CORPORATION

while Fuller' earth and Hazorb were mixed 1:1 with the sludge before being placed in the lysimeter columns. As the results will show, the API Separator sludge existed as a water-in-oil emulsion making it difficult to determine the exact oil content in each lysimeter before extraction.

The loaded lysimeter columns were suspended from a wall rack in the laboratory. Each column was charged with 1000 mL of minimal salts medium and 50 mL of an oil degrading microbial consortium maintained at NHRC. The columns were run at ambient temperature of about 20 degrees. The effluents from the columns were recirculated into the top of the columns using peristaltic pumps equipped with Tygon tubing (0.32 cm ID). Each column contained approximately 100 mL free liquid that was replenished periodically to maintain constant volume. The apparatus is shown in Figure 3. Oclansorb heat treated peat was obtained from Hi Point Industries, Calgary, Alberta. Biosorb heat treated peat was obtained from BIOSORB Technologies Inc., Calgary, AB. Hazorb was obtained from Leavitt Safety Ltd., Calgary, AB. Fuller's earth was obtained from Fisher Scientific.

3.2 Microbial Analyses

Analyses of hydrocarbon degrading microbes in the bioreactor and the lysimeter columns were performed by the most probable number (MPN) technique (3). Samples of the matrix were serially diluted in triplicate from 10^{-1} to 10^{-10} in minimal salts medium. Minimal salts medium contained per Litre:

$K_2HPO_4.3H_2O$	13.1 g
$NaH_2PO_4.H_2O$	5.75 g
NH_4NO_3	2.0 g
$MgSO_4.7H_2O$	0.315 g
$CaCl_2.2H_2O$	0.0006 g
$FeSO_4.7H_20$	0.001 g
Distilled water	1 L

Final pH = 6.8

The medium was dispensed 4.5 mL per tube. After the tubes were inoculated, 50 microlitres of Amauligak crude oil was added to each tube of minimal medium. Organisms capable of metabolizing the oil for growth caused an increase in turbidity and dispersed the oil.

3.3 Water Analyses

Elemental analysis of the leachate and "makeup" waters in the bioreactor were performed at Husky Oil's

© 1991 NOVA HUSKY RESEARCH CORPORATION

Lloydminster laboratory using procedures based on ASTM and standard laboratory methods (Appendix 1). The presence of polyaromatic hydrocarbons in the leachate of the bioreactor was performed by Core Laboratories, Calgary Alberta. PAH's were analyzed by the EPA 625 method after extraction from the water with dichloromethane. Analysis was on an HP 5890 gas chromatograph and an HP 5970 mass spectrometer.

MICROTOX toxicity testing of the bioreactor matrix was performed by Chemex Labs Alberta Inc., Edmonton, AB. and by the Energy Resources Conservation Board (ERCB) lab at Calgary, AB. Solid matrix was mixed 1:5 with distilled water and incubated at room temperature for 3 hours. The water phase was removed by filtration and subjected to toxicity testing.

3.4 Analysis of Extracted Oil

Samples (50 - 100 grams) of the material in the bioreactor were extracted for six hours by the technique of Dean and Stark (Appendix 2) using hot toluene. This time was adequate based on prior experiments with longer refluxing times. The extracted oil was rotary evaporated to remove the toluene and the residue was weighed. The ratio of extracted oil to solids was calculated. These ratios were compared to the ratios obtained at the start of the study enabling a calculation of percent oil loss over the period of study. A 30 mg sample of the dried extracted oil was dissolved in 1 mL of carbon disulfide and subjected to gas chromatography in order to obtain a characteristic fingerprint of the oil and show how the patterns changed as degradation progressed.

For the lysimeter experiments the entire apparatus was subjected to toluene extractions by the technique of Dean and Stark (Appendix 2) until the solvent is clear. Extraction time was variable depending on the concentrations of oil in the matrix. The normal time was sixteen hours. This was performed by Core Laboratories Ltd.

Gas chromatography was performed with a Perkin Elmer Sigma 2000 gas chromatograph equipped with an SPB-5 fused silica capillary column (30m X 0.3 mm ID). The head pressure of the column was 75 kiloPascals and the splitter gas flow was 30 mL/min. The purge gas flow was 3 mL/min. The injector and detector temperature was 320 degrees. The instrument was programmed to run at 70 degrees, followed by a 3 degree per minute increase up to 300 degrees. The temperature was maintained at 300 degrees for 30 minutes. A one microlitre sample was used for injection.

Gas chromatography / mass spectrometry was performed on a Hewlett Packard 5890/5970 gas chromatograph mass spectrometer equipped with a DB-1 column (30 m length, 0.25 mm ID). The carrier gas was helium. The column head pressure was 100 KPascals. The linear velocity was 30 cm/second with a split ratio of 12:1. The instrument was programmed to run at 50 degrees for 2 minutes followed by

© 1991 NOVA HUSKY RESEARCH CORPORATION

10 degree per minute increase up to 300 degrees and then kept constant at 300 degrees for 20 minutes. The injector and detector temperatures were 310 and 250 degrees, respectively. The mass selective detector was scanned from 30 to 500 atomic mass units.

3.5 Flammability Testing of Bioreactor Matrix

Flammability testing was performed according to the method reported in the Canada Gazette Part II, Vol. 122, No. 2, Schedule V, pg. 586 (Appendix 3). The flame source was a cigarette lighter whose flame height was adjusted to that of a 1 inch candle.

4.0 RESULTS

4.1 The Bioreactor

4.1.1 Microbial Numbers in the Bioreactor

The bioreactor maintained high numbers of oil degrading organisms up to eight months. These organisms were capable of growing on a range of aromatic compounds containing up to five fused rings (Figure 4). Microbial numbers fell off sharply in both sections of the bioreactor at nine months (September, 1990) (Figure 5). At this time the water fraction from the bioreactor did not support growth of an added oil degrading microbial population unless phosphate was added also, implying available phosphorus was lacking in the bioreactor. Microbial numbers returned to normal levels at 10 - 11 months (October, November, 1990) but fell again at 15 months (March, 1991). At this time the water fraction in the bioreactor inhibited growth of an oil degrading microbial population. The nature of the inhibition was not determined. Additional wastes may have been dumped into the bioreactor without the knowledge of the present study. In March 1991, the bioreactor was reinoculated with an oil degrading population whose numbers remained high at 21 months in both the API Separator sludge and the Filter press aid sections of the bioreactor (Figure 5).

4.1.2 Water Analysis of the Bioreactor

Table 1 shows large variations in the bioreactor water chemistry over the course of the experiment. Most of this variation can be attributed to addition of fertilizer to the bioreactor. In September, ten kilograms of urea and one kilogram of super phosphate (Appendix 4) were added in an attempt to return the nutrient levels to a C:N:P ratio of 100:10:1. The analysis shows corresponding increases in ammonia but no increase in phosphate. In December, in another attempt to maintain a 100:10:1 ratio, 500 grams of potassium phosphate buffer was added with six kilograms of potassium nitrate. This is reflected by the

© 1991 NOVA HUSKY RESEARCH CORPORATION

increased potassium, nitrate, and phosphate concentrations in the sump samples.
Concentrations of sodium, sulfate and bicarbonate ions increased greatly in the August 1990 sample while phosphate was depleted. This correlates with the first loss of microbial numbers in the bioreactor. The pH of the water was 8.2 compared to an input pH of 7.8 (Table 2). At this time there was an increase in the level of toluene in the volatiles above the bioreactor (Figure 6). This observation is very odd and has never been explained.

By March 1991, the pH of the sump had returned to 6.7 (Table 2). However, the sodium and sulfate ion concentrations remained high. In addition, there was a significant increase in the levels of nitrate and potassium ions. This coincided with the second loss of oil degrading bacteria in the bioreactor but no true correlation was proven. No volatiles were assayed at this times.

4.1.3 Oil Contents of the Bioreactor

While the bioreactor ran for a total of 21 months and microbial numbers fluctuated over this period, there was no further increase in oil degradation over that observed at eight months for the API separator sludge (Table 3). Oil degradation in the filter press aid increased from 62% to 76%.

4.1.4 Flammability of Bioreactor Contents

The bioreactor matrix proved not to be a flammable solid. This designation requires the substrate to burn within 5 seconds after holding a 1" candle to it. The bioreactor matrix would burn only in the presence of a blue flame from a Bunsen burner. When the Bunsen burner flame was removed, continued burning of the matrix was of short duration. The residual flame on the matrix travelled at a rate of 1 cm/30 seconds. This type of flame is identified as a smolder. The bioreactor matrix is therefore a nonflammable solid.

4.1.5 Characteristics of the Bioreactor Contents

The water/leachate from the bioreactor does not contain PAH's, or hydrocarbons (Table 4). The levels of priority pollutants found in the sump water and in the solid material from the bioreactor were compared to the regulated levels in Table 5. The sump water is the accumulated leachate from the bioreactor from 1.6 years' operation. The low levels of materials present indicate that priority pollutants are not being released at legislated levels. Because of the low levels of priority pollutants in the solid material and the heap leach nature of the bioreactor, it was deemed not necessary to perform the Canadian General Standards Board 164-GP-IMP leachate extraction procedure (Appendix 5).

The oil extracted from the bioreactor matrix was a solid, tarry material. It did not support further significant microbial growth in laboratory tests. The solid matrix was not combustible, was not leachable,

was low in heavy metals and had a high asphaltene content (Table 6) and is therefore landfillable (Appendix 6).

Toxicity of materials can be determined by a formula proposed in the Transport of Dangerous Goods Act, Sec. 3.19 (Appendix 7). However, because of the large number of potential compounds and their low concentrations, a toxicity test was performed instead. A MICROTOX test was chosen for its reproducibility, rapidity, and good correlation with other toxicity tests (17). The results shown in Table 7 indicate that the leachables from the bioreactor matrix are marginally toxic.

A UV scan of the yellow coloured leachate from the bioreactor matrix showed an absorption peak at 200 - 260 nm. Extraction of the leachate in 1-butanol at pH 2.0 removed the UV absorbing material and the yellow color. Infrared spectroscopy of the extracted material indicated the presence of organic carboxylates (Figure 7). The infrared spectrum was similar to that of authentic humic acid (Figure 7). When redissolved in water this material had an acid pH of 3.3. When the pH was neutralized this material had a medium toxicity in the MICROTOX test (Table 7). It thus appeared that the toxicity of the leachate from the bioreactor matrix resided in the humic acids leached from the peat in the matrix.

4.2 Lysimeter Columns

4.2.1 Physical Appearance of the Lysimeter Columns

When the Hazorb/sludge mixture came in contact with water in the lysimeter columns, the oil separated from the Hazorb and floated on the surface of the water (Figure 8). Its use was discontinued after three weeks. The lysimeter containing Fuller's Earth initially had normal flow rates. In less than one month of operation the glass frit at the bottom of the recirculating column sealed off and no further flow took place. The recycled Oclansorb from the Lloydminster bioreactor did appear to compact somewhat in the lysimeter column. However, this did not inhibit liquid flow through the column. All the other columns had satisfactory flow rates and did not show evidence of compacting.

In some columns a biofilm could be observed exuding from the bottom of the column (Figure 9). Biofilms were observed in all columns with the most extensive biofilms found in the lysimeters containing recycled bioreactor matrix and 2:1 oily sludge/Oclansorb ratios.

4.2.2 Microbial Numbers in Lysimeter Columns

High numbers of hydrocarbon degrading bacteria were observed after 60 days in all the lysimeter columns (Table 8). Since use of the column containing Hazorb was discontinued after 3 weeks microbial numbers in this column were not monitored.

With the columns containing Oclansorb, microbial numbers increased with increased sludge loading (Table 8). At the higher sludge/Oclansorb ratio microbial numbers appeared to be relatively constant throughout the lysimeter column as attested by microbial frequencies at the top and bottom of the columns.

The reused Oclansorb from the Lloydminster bioreactor contained higher numbers of oil degrading bacteria than the fresh Oclansorb at the same sludge loading ratios (1:1) (Table 8). While the columns containing Biosorb and Fuller's earth contained high oil degrader numbers in the top of the reactor, those columns did not have sampling ports in the bottoms of the columns and so could not be sampled in that area.

4.2.3 Oil Contents of Lysimeter Columns

Oil contents in the lysimeter columns did not correlate with sludge loadings. The columns containing API Separator sludge/Oclansorb ratios 1:1, 2:1, 3:1 and 4:1 did not have initial oil contents to match these ratios (Table 9) due to the variable oil content of the API Separator sludge. For example, the 4:1 ratio contained oil/Oclansorb of only a 1:1 ratio. The most oil (79 grams or 22%) was lost in the column containing the 2:1 ratio of sludge/Oclansorb (Table 10) during a two month period. The column containing the reused bioreactor matrix initially contained 1.66:1 ratio of oil/Oclansorb (Table 9). This had reasonable degradation of 11% - 15% (27 grams oil loss) (Table 10) during a two month period.

The column containing API separator sludge/Fuller's Earth at a 1:1 loading ratio actually contained 0.37:1 ratio of oil/Fuller's Earth (Table 9). This column had the least oil loss of 3% (7 grams) over a two month period (Table 10).

Columns containing Biosorb at 1:1 and 4:1 API separator sludge/absorbent ratios actually contained 0.56:1 and 1.8:1 oil/absorbent ratios (Table 9). Degradation in these columns was 15% (16 grams) and 9% (34 grams) respectively over a two month period (Table 10).

5.0 DISCUSSION

5.1 The Bioreactor

5.1.1 Microbial Numbers in Bioreactor

Compared to original microbial levels, numbers of oil degrading microbes were severely depleted in the bioreactor at nine and fifteen months operation. This contrasts with previous studies where oil degrading numbers consistently remained high over 14 months in laboratory bioreactors at NHRC and 11 months in a field bioreactor established at Prince George (1,4). Loss of microbial numbers correlated with phosphate deficiency, unusual water chemistry and, in one instance, with increased toluene in the volatiles which cannot be explained. That the water from the bioreactor inhibited microbial growth in lab experiments implies that toxics were accumulating in the bioreactor or that the source of the inhibition is external. It is possible that additional slop oil and other wastes containing such constituents as toluene were deposited in the bioreactor without the knowledge of this study. The contents of these wastes could have adverse effects on the oil degrading population in the bioreactor.

5.1.2 Oil Content of The Bioreactor

The oil content of the API separator sludge section of the bioreactor did not show a significant additional decrease over the levels present at eight months. The oil in the section of the bioreactor containing the filter press aid was a relatively light oil fraction which continued to degrade at a reduced rate. Up to 76% of the original oil had degraded by 21 months. In contrast the oil in the section of the bioreactor containing the API Separator sludge was much heavier and only 46% degradation was obtained. These observations confirm that the lighter oil fractions are more readily degraded and the complex molecules in the higher fractions degrade much more slowly over time. Lack of significant increased degradation over the prolonged period of study indicates the extent of degradation achievable in the bioreactor. The tarry characteristic of the remaining oil indicates that it no longer contains biodegradable light ends. This is supported by lack of microbial growth on the oil recovered from the bioreactor in lab studies. Characterization of the oil degrading population in the bioreactor showed a lack of asphaltene degraders and this correlates with increasing asphaltenes in the residual oil. Microbial growth on asphaltenes is rare and there are few reports of microbial growth on this material (5,6). Additional degradation might be achieved by a chemical oxidation step followed by further microbial treatment. Work performed at the Institute of Gas Technology for the Gas Research Institute has demonstrated increased microbial degradation of PAHs after chemical oxidation with peroxide or Fenton's reagent (14).

5.1.3 Disposal of Bioreactor Contents

The water fraction from the bioreactor does not contain oil, PAHs, or heavy metals. It may be disposed of along with normal refinery water wastes or by deep well injection. The leachates from the bioreactor matrix were marginally toxic based on the MICROTOX toxicity assessment system. This was unexpected as both solids and leachate from the bioreactor contain much less than the regulated levels of contaminants. PAH compounds, which are known to be toxic, were not present in the leachates from the bioreactor. Under bioremediation conditions PAHs present in diesel spilled on soil reportedly were destroyed and lost toxicity within a 20 week period (18). Toxicity in the bioreactor contents was traced to humic acids present in the leachate waters. The source of the humic acids may be the peat absorbent or the heavy oil. Extracts of Oclansorb and of locally available peat contained humic acids. Humic acids from Athabasca oil sand bitumen have been characterized (19). Humic acids are normal soil components and are not normally considered toxic. However, there may be other undetected organic compounds, products of hydrocarbon metabolism, present in the leachate water which acting alone or in combination with the humic acids are inhibitory to the *Photobacterium phosphoreum* test organism used in the MICROTOX system. The organisms growing on oil in the bioreactor or on the original peat may also produce antibiotic substances which are inhibitory to the *P. phosphoreum*.

Additionally, although the MICROTOX system has good correlation with other toxicity tests (17), it does present a few anomalies. MICROTOX is liable to inhibition by any inhibitor of the electron transport chain. It is affected by heavy metals at concentrations as low as 1 mg/L (Mr. Charles Walbourn, MICROBICS Corporation, Carlsbad, CA; Personal Communication) (Appendix 8). Materials which have been found to be toxic by the MICROTOX assay include bicarbonates and extracts of wood chips, hay and straw (Dr. Steve Davies, Alberta Environmental Centre, Vegreville, Alberta; Personal communication). Additionally, potentiation effects due to synergy between combinations of contaminants have been reported (15). While regulated contaminants in the matrix and leachate are below toxic levels, combinations of contaminants may make the leachate toxic by the MICROTOX assay. MICROTOX therefore, may be too sensitive an assay for a waste stream containing a combination of contaminants. It has been argued that MICROTOX is most reliable with single contaminant assays but is less reliable in multicontaminant systems (15).

The solids from the bioreactor can be recharged with API separator sludge and replaced in the bioreactor for a second round of biodegradation as was demonstrated in the lysimeter studies. However, ultimate disposal after recycling will still be required.

For ultimate disposal, the solids from the bioreactor containing higher molecular weight species and an oil degrading population, could be used as a soil additive and conditioner to improve soil structure and fertility. Agriculture Canada has been conducting ongoing research to utilize oily waste sludge to

© 1991 NOVA HUSKY RESEARCH CORPORATION

conserve and improve the structure of sandy, cultivated soils and increase their humic content (7). Results obtained over a three year study period show sludge incorporation greatly improved the soil's structure through large and persistent increases in primary and secondary aggregation. It also effected beneficial increases in soil microbial activities and populations. Humic materials were also increased in the sandy soils (V.O. Biederbeck, Agriculture Canada, Regina, Saskatchewan; personal communication).

A negative effect of employing hydrocarbon for this treatment was phytotoxicity to cereal grain production but this could be prevented by increased fertilization (7). Negative effects on vegetation might also be avoided by the presence of Oclansorb. Studies performed by NHRC at a landfarm at Husky Oil's Prince George refinery showed that Oclansorb stimulated oil degradation in test plots and it also caused an increase in vegetation regrowth in the test plots (9,10). The quantity and variety of revegetation was increased when Oclansorb was placed with oily sludge in test plots. Independent work conducted at the University of Calgary's Kananaskis Center for Environmental Research established that barley crops grown in soil containing oily sludge did not accumulate compounds attributable to the organics originating in the sludge (8). It thus appears that the technique of using oily sludge materials to aggregate soils does not pose an environmental threat. However, using bioreactor matrix for such an application may prove difficult due to public perceptions about the nature and quality of oily waste.

Another disposal option is to place the spent matrix on a landfarm. It will seed the site with an already adapted, active oil degrading population. Studies have already attested to the superior oil degradation rates achieved with Oclansorb in a landfarm (9). An additional bonus is that plots treated with Oclansorb showed increased quantity and variety of vegetation regrowth (10). However, since the residual matrix from the bioreactor has a high asphaltene content, continued application on a landfarm site might overload it with a hard to degrade oil fraction. Asphaltenes do biodegrade in soil but rates are low (8,11). Therefore continued application of spent matrix may result in accumulation of asphaltenes. Loading on a landfarm could be a one time or, at b7est, infrequent occurrence. Nevertheless, the degradation capacity of or by a combined bioreactor/landfarm may exceed the landfarm alone since much of the degradation occurs in the bioreactor.

A third disposal option is to landfill the solids. The peat matrix has already been subject to anaerobic degradation in a peat bog. In an anaerobic landfill it is unlikely to undergo further degradation and hence is unlikely to release any adsorbed hydrocarbons or metals. The hydrocarbons adsorbed to the matrix are large inert molecules which are also unlikely to undergo further degradation in the anaerobic landfill. This results in low residual liability for the waste generator.

Within Alberta there are industrial landfills and municipal landfills. Hydrocarbons normally are banned from Alberta municipal landfills and so the spent bioreactor matrix would be directed to an industrial landfill. In Saskatchewan hydrocarbon materials are banned from landfills. However, exceptions to these regulations may be obtained by special order of the Minister of Environment after certain condition/standards have

© 1992 NOVA HUSKY RESEARCH CORPORATION

been met. They are determined for each case after thorough examination of the proposed landfill materials and negotiations with the individual landfill operator. The bioreactor matrix consists of a non-hazardous solid (Oclansorb) used to adsorb hazardous waste (oil). Because the oil will not separate as a liquid from the peat, the matrix is now classified as a solid waste. Documentation was prepared attesting that the bioreactor residue is not hazardous based on leachability, toxicity and flammability. This documentation was presented to the landfill operator at Lloydminster, Saskatchewan and to the Saskatchewan Department of Environment and Public Safety. This department reviewed the documentation. It agreed that the material might be acceptable at a municipal landfill in Saskatchewan. However, since the Lloydminster landfill does not have a liner, the department cannot recommend that the bioreactor residue be placed there. Discussions with the department are ongoing.

5.2 Lysimeter Columns

5.2.1 Physical Appearance of Lysimeter Columns

Over the period of the study, the matrix in all the lysimeters compacted somewhat. However, with the exception of the one containing Fuller's Earth, all the columns still allowed free percolation of the liquid and thus there appeared to be adequate aeration as indicated by the high numbers of oil degraders at the top and the bottom of the columns.

The lysimeter column containing the reused matrix from the Lloydminster bioreactor appeared to compact the most. This may be due to water absorption by the Oclansorb as this column retained the most water. Examination of the Oclansorb after oil extraction showed no difference in texture from that present in the other columns.

Hazorb is sold as a general absorbent for spills. During absorption, the spilled liquid is taken up by the bulk of he sorbent material. Electron microscopic examination of Hazorb and Oclansorb have established that they are both highly porous making them excellent absorbents for hydrocarbons (16). However, Hazorb is not hydrophobic and unlike Oclansorb it does not preferentially retain hydrocarbons. This is why the oil was not retained by the matrix in the lysimeter column containing Hazorb. It cannot be an effective matrix for hydrocarbon degradation.

5.2.2 Microbial Numbers and Oil Degradation in Lysimeter Columns

High numbers of oil degrading bacteria were observed in all the lysimeter columns after two months attesting to the effectiveness of the absorbents in retaining the oil and serving as support for microbial growth. Oclansorb showed increased microbial numbers with increased sludge content implying that the microbes were growing on the oil. However, there was less oil present at higher sludge loadings and less oil degradation. Unfortunately, microbial numbers were not monitored over the whole period of the study

© 1992 NOVA HUSKY RESEARCH CORPORATION

so there is no information available on population shifts within this time period. Since the recycled bioreactor matrix, 1:1 and 2:1 sludge/Oclansorb loadings first showed evidence of biofilms leaching out of the columns, it is possible that these columns contained higher oil degrading numbers earlier in the study and the numbers had declined by two months to match those present in the columns containing more sludge but less oil.

The initial oil contents of the Lysimeter columns do not correlate with the sludge loading rates. This can be attributed to separation of the oil from the water in the sludge on standing. When the columns were prepared the 1:1 and 2:1 Oclansorb columns were prepared first and so received mostly oil from the top of the sludge sample. Columns prepared after these two received more emulsified sludge containing less oil and proportionately more water.

The most oil degradation was obtained in the lysimeter columns containing 1:1 and 2:1 sludge/Oclansorb. Generally oil losses in the columns appeared to correlate with oil/absorbent ratios (Figure 10) implying that all absorbents were equally effective at promoting degradation and any absorbent is potentially useful or that the columns were not all operating in a comparable fashion. The latter explanation is more likely since the column containing Fuller's earth became plugged and liquid flow ceased after a few weeks. Without liquid flow to transport oxygen throughout the columns, biodegradation will decrease. Because of compacting and plugging, filter press aid alone will not be an acceptable matrix for oil degradation in a bioreactor. Factors affecting degradation rates may include oxygen limitation, water saturation and recycle rate. Attempts were made to keep these constant by employing the same multichannel pump for recycling the liquids in the columns. However, individual differences in sludge loading and matrices suggest that these should be controlled on an individual basis. Inhibitory materials present in the water of the sludge might have curtained initial microbial growth and activity thus hindering oil degradation in some of the columns. It is noteworthy that there was a significant water content of the sludge added to the columns except those containing the 1:1 and 2:1 sludge/Oclansorb ratios which had the most oil degradation. Inhibitory materials present in the water could include scale inhibitors, demulsifiers, biocides and even protozoa. Protozoa were observed in the leachate water from the column containing 4:1 sludge/Oclansorb but not in that from the column containing 1:1 sludge/Oclansorb. Protozoa are known to graze on bacteria as a food source (12).

Since microbial numbers were high at 2 months in the Biosorb columns, increased degradation might have occurred with a longer running time.

No information was collected on evaporative losses from the columns. However, since the oil used in the present study was API Separator sludge, which had already been subjected to considerable weathering, it should not have contained much light material which would have readily evaporated. The lysimeter column studies were performed to assess loading rates and the performance of different absorbents.

© 1991 NOVA HUSKY RESEARCH CORPORATION

There is therefore no attempt to quantitatively compare degradation rates in the lysimeter columns with those obtained in the bioreactor.

5.2.3 Evaluation of Recycled Oclansorb and Other Matrices for Oil Degradation

A preliminary study performed for NOVA's Technology Management Office compared the bioreactor with alternative technologies (13). That study indicated that the cost of the adsorptive matrix was the most costly component of the system. To be competitive with other disposal options like the high volume Taciuk process and Mobil's coking process, the adsorptive matrix would have to be recycled 3 - 4 times and sludge loading would have to be 2:1 sludge/Oclansorb (13). We have demonstrated that the adsorptive matrix can be recycled at least once and sludge: Oclansorb ratios of 2:1 are possible. Considering that the 2:1 ratio used in the present study represented 1.72:1 oil/Oclansorb ratio, and API Separator sludge usually contains about 50% oil (B. Brierley, Husky Oil, Lloydminster; Personal communication), it is possible to achieve a 3.44:1 sludge/Oclansorb loading ratio and still obtain high levels of oil degradation. This puts a bioreactor on a competitive footing with other disposal technologies.

Another source of improvement suggested in the above study was alternative matrices. Fuller's Earth and Biosorb were chosen as possible alternates. Biosorb is a locally produced heat treated peat product similar to Oclansorb. Like Oclansorb, it absorbs up to five times its weight in oil. Because it is produced locally, Biosorb will not be as expensive as Oclansorb whose high cost is due to transportation from High Point Industries' peat plant in Newfoundland. Oclansorb currently sells for $3.03 - $3.58 per Kg while Biosorb sells at $1.816 per Kg. Negotiations for bulk quantities could lower the price of Biosorb. Fuller's earth at $7.48 per Kg would be too costly as an oil absorbent matrix in the bioreactor. Biosorb functions as well as Oclansorb as an oil degrading matrix and its lower price makes the bioreactor an economically competitive technology for treatment of low volume high oil content wastes generated in the area of up to 100 cubic meters per year.

6.0 CONCLUSIONS

1. Loading rates of oil on Oclansorb have been underestimated up to now. Higher rates of loading at least 1.72:1 oil/Oclansorb are possible and still allow significant oil degradation levels.

2. The spent matrix from the bioreactor can be recycled at least once and still allow significant microbial growth and oil degradation.

3. For ultimate disposal the solid matrix from the bioreactor can be placed in a landfill.

© 1991 NOVA HUSKY RESEARCH CORPORATION

4. Biosorb, a locally produced heat treated peat product from Alberta will absorb oil, allow microbial colonization and foster microbial degradation at levels comparable to Oclansorb.

5. Fuller's earth or diatomaceous earth alone may compact and decrease water percolation rates. This will cause a decrease in biodegradation rates. Thus, filter press aid alone will not achieve optimal degradation rates.

6. Hazorb releases absorbed oil on contact with water and is not an appropriate matrix for oil degradation.

7.0 REFERENCES

1. Francis, M. 1989. A Study to Achieve Enhanced Oil Degradation Based on Composting the Oil with a Biomass Product. NOVA HUSKY Research Corporation Report # 00435.

2. Francis, M. McD. and Stehmeier, L.G. 1990. DEGRADATION OF SLUDGES FROM HEAVY CRUDES IN CONTAINED REACTORS: Lloydminster Bioreactor for Sludge Degradation. NOVA HUSKY Research Corporation Report # 00586.

3. Multiple Tube Fermentation Technic for Members of the Coliform Group. In Standard Methods for the Examination of Water and Waste Water. Fifteenth Edition. American Public Health Association, Washington, D.C. Edited by A. Greenberg, J.J. Connors and D. Jenkins 1981. pp. 801 - 805.

4. Francis, M. 1989. Field testing of Oily Sludge Degradation in a Reactor. NOVA HUSKY Research Corporation Report # 00448.

5. Bertrand, J.C.; Rambeloarisoa, E.; Rontini, J.F.; Guisti, G. and Mattei, G. 1983. Microbial degradation of crude oil in sea water in continuous culture. Biotechnol. Lett. 5: 567 - 572.

6. Gerson, D.F.; Zajic, J.E.; Cooper, D.G. and Ouchi, M.D. 1977. Microbial Separation of Bitumen from Athabasca Tar Sand Part II. Biochemical Engineering Research Reports, Volume II. Biochemical Engineering Faculty of Engineering Science, University of Western Ontario. pp 190 - 198.

7. Biederbeck, V.O. 1990. Using oily waste sludge disposal to conserve and improve sandy cultivated soils. First International Symposium on Oil and Gas Exploration and Production Waste

© 1991 NOVA HUSKY RESEARCH CORPORATION

Management Practices. New Orleans, LA. Sept. 10 - 13, 1990.

8. Danielson, R.M., Okazawa, N. and W.J. Ceroici. 1989. Disposal of oilfield wastes by landtreatment: Effects on the environment and implications for future land use, 1988 Research Report. Canadian Petroleum Association and Environment Canada.

9. Francis, M. 1988. Peat Augmented Landfarming. NOVA HUSKY RESEARCH CORPORATION Report Number 00330.

10. Francis, M. McD. 1988. LANDFARMING OF OILY WASTES: Enhancing Degradation by Specific Amendments. In Proceedings of the Fifth Annual General Meeting of BIOMINET. November 2, 1988. Calgary, Alberta. Edited by R.G.L. McCready. pp 119 -127.

11. Bulman, T.L.; Lesage, S.; Fowlie, P.G.A. and Webber, M.D. 1985. The Persistence of Polynuclear Aromatic Hydrocarbons in Soil. PACE Report No. 85-2. 51 pp.

12. Gurijala, K.R. and Alexander, M. 1990. Explanation for the decline of bacteria introduced into lake water. Microbial Ecology 20: 231 - 234.

13. Kearns, I. 1991. BIOREACTOR: Feasibility Study. NOVA HUSKY RESEARCH CORPORATION Report Number 00649.

14. Gauger, W.K.; Kilbane, J.J.; Kelley, R.L. and Srivastava, V.J. 1990. Enhancement of microbial degradation of hydrocarbons in soil and water. In Gas, Oil, Coal, Environ. Biotechnol. 2. Edited by C. Akin and J. Smith. Institute of Gas Technology, Chicago, IL. pp 171 - 203.

15. Qureshi, A.A.; Coleman, R.N. and Paran, J.H. 1984. Evaluation and refinement of the microtox® test for use in toxicity testing. In TOXICITY SCREENING PROCEDURES USING BACTERIAL SYSTEMS. Edited by D. Liu and B.J.Dutka. Marcel Dekker, Inc. New York and Basel. pp 1 - 22.

16. Francis, M. McD.; Gerlich, M.; Geise, T. and Stehmeier, L.G. 1990. DEGRADATION OF SLUDGES FROM HEAVY CRUDES IN CONTAINED REACTORS: Fate of Hydrocarbons Absorbed to Oclansorb. NOVA HUSKY Research Corporation Report # 00555.

17. Bulich, A.A. 1986. Bioluminescence Assays. In Toxicity Testing Using Microorganisms. Edited by G. Bitton and B.J. Dutka. CRC Press Inc. Boca Raton, Florida. pp 57 - 74.

18. Wang, X., Yu, X. and Bartha, R. 1990. Effect of bioremediation on polycyclic aromatic

© 1991 NOVA HUSKY RESEARCH CORPORATION

hydrocarbon residues in soil. Environmental Science and Technology 24: 1086 - 1089.

19. Majid, A.; Sparks, B.D. and Ripmeester, J.A. 1991. Characterization of humic acids from sludge pond solids. In Volume 36, No. 3, Preprints of Papers Presented at the 202nd ACS National Meeting, New York, NY. August 25-30, 1991. pp 1354 - 1360.

© 1991 NOVA HUSKY RESEARCH CORPORATION

8.0 TABLES

© 1991 NOVA HUSKY RESEARCH CORPORATION

TABLE 1: CATION AND ANION ANALYSIS OF THE BIOREACTOR WATER

DATE	ION CONCENTRATION (mg/L)													
(1990)	MONTH	Na^{+}	K^{+}	NH_4^{+}	Mn^{+2}	Ca^{+2}	Mg^{+2}	Fe^{+3}	Cl^{-1}	HCO_3^{-1}	CO_3^{-2}	NO_3^{-1}	SO_4^{-2}	PO_4^{-3}
January 19	1	405	455	347	2	69	52	0.2	953	366	0	ND	1103	1151
March 19	3	440	121	ND	4	102	77	1.3	136	380	0	203	844	59
April 2	4	370	77	ND	3.4	86	61	2.8	107	385	0	65	787	77
April 16	4	416	73	ND	2.8	78	60	2.5	114	424	0	ND	854	68
May 28	5	330	49	ND	2.6	79	59	2.2	77	541	0	8	603	29
June 13	6	470	68	ND	3.8	103	85	0.9	103	634	0	4	958	35
August 15	8	1085	106	ND	4.7	341	156	1.2	261	1097	0	0.1	2242	0
September 17	9	886	80	953	0.1	52	117	0.2	212	2852	36	6.6	2141	0
October 16	10	689	72	1158	1.7	47	35	1.7	198	2950	0	22	2114	0
November 14	11	814	86	850	1.1	45	49	2.0	250	1341	0	50	2638	38
December 14	12	873	4330	708	2.6	105	106	1.7	215	878	0	7565	2163	664
(1991)														
January 22	13	1526	3840	692	4.2	127	166	2.0	399	975	0	5764	2869	291
February 22	14	874	839	390	5.5	213	170	0.4	184	585	0	2029	2022	126
March 26	15	930	940	ND	3.7	250	186	1.1	215	351	0	1905	2080	0
September 23	21	1516	970	ND	6.8	408	288	0.2	372	332	0	2860	3197	19

© 1991 NOVA HUSKY RESEARCH CORPORATION

TABLE 2: pH OF THE BIOREACTOR LEACHATE			
SAMPLING TIME	pH		
DATE	MONTH	FEED	LEACHATE
June 13, 1990	1	8.2	7.5
August 15, 1990	8	7.8	8.2
September 17, 1990	9	8.3	8.5
October 16, 1990	10	7.4	8.2
November 14, 1990	11	7.5	7.4
December 14, 1990	12	7.8	7.0
January 22, 1991	13	7.8	6.7
February 22, 1991	14	-	6.3
March 26, 1991	15	-	6.6
September 23, 1991	21	7.3	7.4

© 1991 NOVA HUSKY RESEARCH CORPORATION

TABLE 3: OIL CONTENT IN THE BIOREACTOR								
SAMPLING TIME	API SEPARATOR SLUDGE				FILTERPRESS AID			
	OIL	SOLIDS	OIL/SOLIDS	% OIL LOSS	OIL	SOLIDS	OIL/SOLIDS	% OIL LOSS
January 1990 (start)	140	182	0.77	0	35	167	0.21	0
August 1990 (8 months)	81	195	0.42	46	17	218	0.08	62
September 1991 (21 months)	44	105	0.42	46	7	150	0.05	76

© 1991 NOVA HUSKY RESEARCH CORPORATION

TABLE 4: PAH CONTENTS OF THE BIOREACTOR LEACHATE	
COMPOUND	**CONCENTRATION (microgram/Liter)***
Napthalene	<1
Acenaphthylene	<1
Acenaphthene	<1
Fluorene	<1
Phenanthrene	<1
Anthracene	<1
Fluoranthene	<1
Pyrene	<1
Benzo (a) anthracene	<1
Chrysene	<1
Benzo (b) fluoranthene	<1
Benzo (k) fluoranthene	<1
Benzo (a) pyrene	<1
Indeno(1,2,3-cd) pyrene	<1
Dibenzo (a,h) anthracene	<1
Benzo (g,h,i) perylene	<1
Oil	<1

* A detection limit of 1 microgram/L was used based on a water sample of 1 L. This water was sampled after eight months running time.

© 1991 NOVA HUSKY RESEARCH CORPORATION

TABLE 5: PRIORITY POLLUTANT LEVELS FOUND IN THE BIOREACTOR MATRIX					
	CONCENTRATION*[a]			REGULATED LEVELS*[b]	
SPECIES	SLUDGE	FILTER PRESS AID	SUMP	SOLIDS	EXTRACTS
Arsenic	<10	<10	<0.1	500	5
Barium	110	99	0.079	-	100
Benzene	ND	ND	ND	1000	0.07
Boron	<1	<1	<0.1	-	500
Cadmium	0.6	<0.5	<0.002	100	0.5
Chromium	10	7	0.006	500	5
Lead	15	7	<0.03	500	5
Mercury	0.015	0.017	<0.001	100	0.1
Nickel	12	6	0.02	134	-
Nitrate	-	-	0.9	-	1000
Nitrite	-	-	0.9	-	1000
Selenium	<5	<5	<0.05	100	1
Silver	<1	<1	<0.005	-	5
Toluene	ND	ND	ND	1000	14.4
Thallium	<10	<10	<0.1	130	-
Xylene	ND	ND	ND	1000	-

* mg/liter or kilogram
\- No Regulatory Level Found
ND None detected
a August 15, 1990 samples (eight months running time)
b Lowest levels round in the transportation of Dangerous Goods Act, Toxicity Characteristic Leachability Procedure, and Guide for Waste Managers

© 1991 NOVA HUSKY RESEARCH CORPORATION

TABLE 6: ASPHALTENE CONTENT OF THE BIOREACTOR		
SAMPLE TIME	BIOREACTOR SAMPLE	
	API SEPARATOR SLUDGE	FILTER PRESS AID
START	14	4
8 MONTHS	26	20
21 MONTHS	26	20

* Asphaltenes are defined as pentane precipitate materials.

© 1991 NOVA HUSKY RESEARCH CORPORATION

TABLE 7: MICROTOX TEST FOR TOXICITY OF BIOREACTOR MATRIX FROM THE API SLUDGE AND FILTER PRESS AID AREAS

SAMPLE	TOXICITY (EC50) *
Bioreactor Matrix Leachate (Sample 1)	55.7
Bioreactor Matrix Leachate (Sample 2)	77.6
n-Butanol Extract of Bioreactor Matrix Leachate**	41.0
Water Fraction of Bioreactor Leachate after n-Butanol Extraction	100
Oclansorb Peat Leachate*	40.8
Distilled Water	+

* The EC50 is defined as the concentration of the original sample which would cause 50% inhibition of the light emission in the MICROTOX assay.

\+ Had no significant effect on the MICROTOX assay.

** Humic acids were traced to n-butanol extracts of water leachates of Oclansorb, bioreactor matrix and commercially available garden peat.

© 1991 NOVA HUSKY RESEARCH CORPORATION

TABLE 8: OIL DEGRADING MICROBES IN THE LYSIMETER COLUMNS AFTER TWO MONTHS OPERATION		
OIL ABSORBENT	**OIL DEGRADING MICROBES PER GRAM**	
	TOP OF COLUMN	**BOTTOM OF COLUMN**
OCLANSORB (RATIO) +		
1:1	8.6×10^5	3.0×10^5
2:1	4.2×10^6	8.6×10^4
3:1	8.6×10^6	1.86×10^7
4:1	4.6×10^8	$>4.6 \times 10^8$
REUSED OCLANSORB (RATIO) +		
1:1	1.86×10^8	3.0×10^7
BIOSORB (RATIO) +		
1:1	$>4.6 \times 10^8$	ND*
4:1	$>4.6 \times 10^8$	ND*
FULLERS EARTH (RATIO) +		
1:1	$>4.6 \times 10^8$	ND*

+ The ratio is the ratio of API Separator sludge to the matrix on a weight basis.

* ND - not determined.

© 1991 NOVA HUSKY RESEARCH CORPORATION

TABLE 9: INITIAL OIL CONTENTS OF LYSIMETER COLUMNS					
	WEIGHT OF MATRIX IN COLUMN	COMPOSITION			
		OIL	WATER	SOLID	RATIO (OIL:OCLANSORB)
OCLANSORB					
1:1	442	208	50	184	1.13
2:1	657	365	80	212	1.72
3:1	822	244	386	192	1.27
4:1	960	181	600	179	1.01
BIOSORB					
1:1	461	108	160	193	0.56
4:1	820	370	244	205	1.80
FULLER'S EARTH					
1;1	1361	250	435	676	0.37
RECYCLED OCLANSORB					
1:1	1460	245	1067	148	1.66

© 1991 NOVA HUSKY RESEARCH CORPORATION

TABLE 10: OIL LOSSES OVER IN GRAMS AND AS A PERCENTAGE OF INITIAL LOADING IN LYSIMETER COLUMNS OVER TWO MONTHS OPERATION AT ROOM TEMPERATURE

	OIL CONTENT		DECREASE	% OIL LOSS
	START	END		
OCLANSORB				
1:1	208	172	36	17
2:1	365	286	79	22
3:1	244	239	6	2
4:1	181	173	8	4
BIOSORB				
1:1	108	92	16	15
4:1	370	336	34	9
FULLER'S EARTH				
1:1	250	243	7	3
RECYCLED OCLANSORB				
1:1	245	218	27	11*
	(175)	(148)	27	(15)

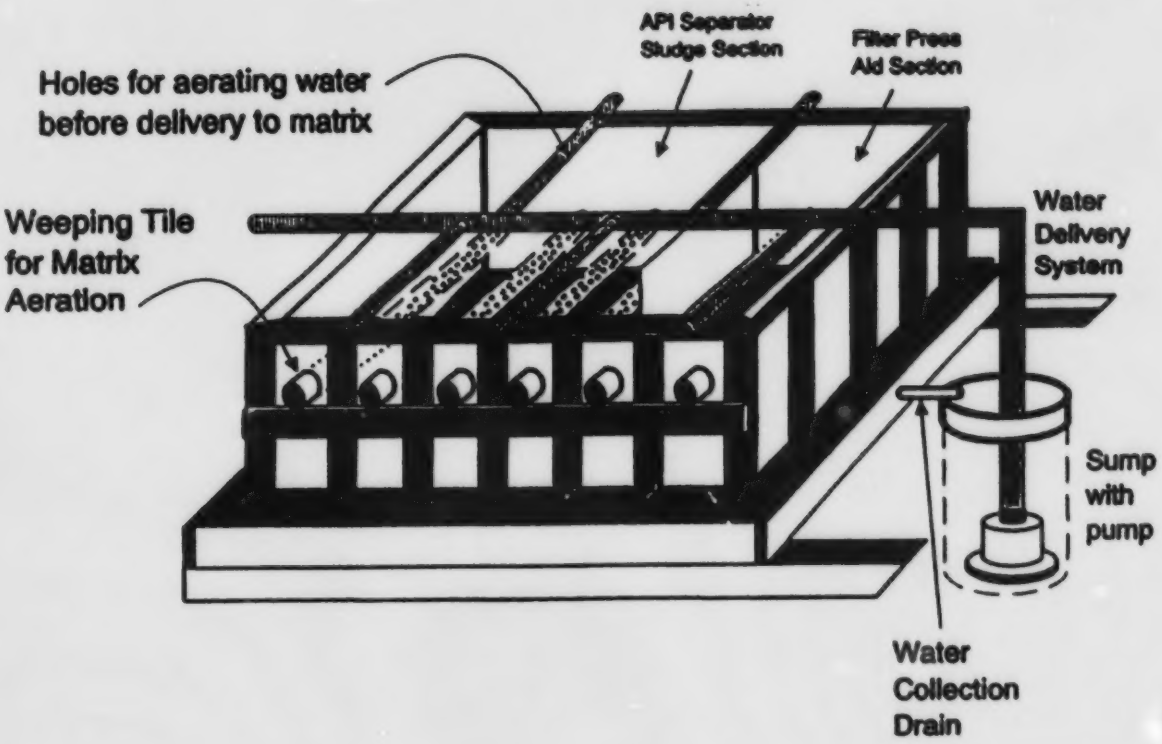
* The recycled Oclansorb matrix from the bioreactor used in that particular lysimeter column already contained 69.8 grams of oil. This oil is non degradable as was demonstrated in shake flask studies. Correcting for the presence of this non degradable oil in the sample, the amount of degradation of the additional oil from the API Separator sludge is 15%.

© 1991 NOVA HUSKY RESEARCH CORPORATION

9.0 FIGURES

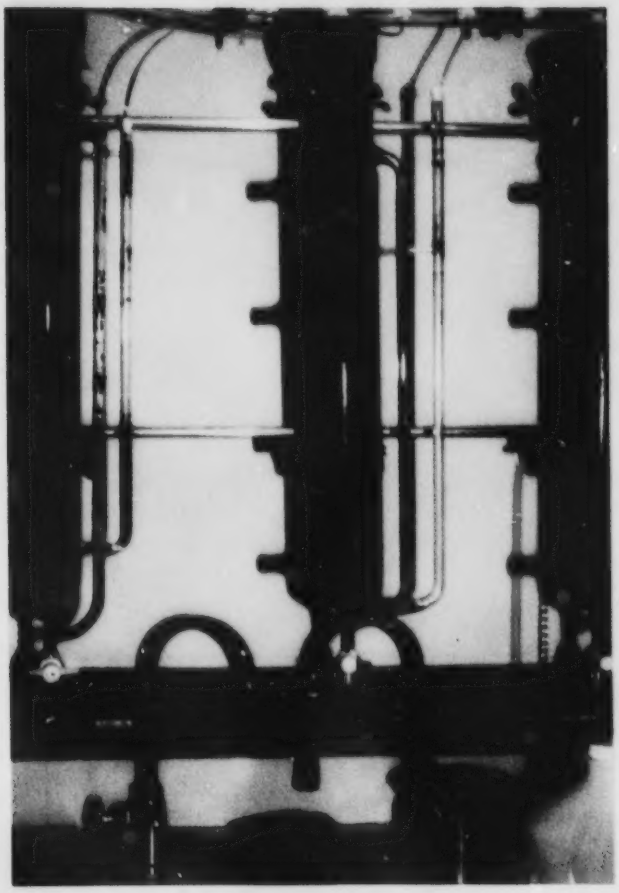
© 1991 NOVA HUSKY RESEARCH CORPORATION

FIGURE 1. THE BIOREACTOR



© 1991 NOVA HUSKY RESEARCH CORPORATION

FIGURE 2. A LYSIMETER COLUMN

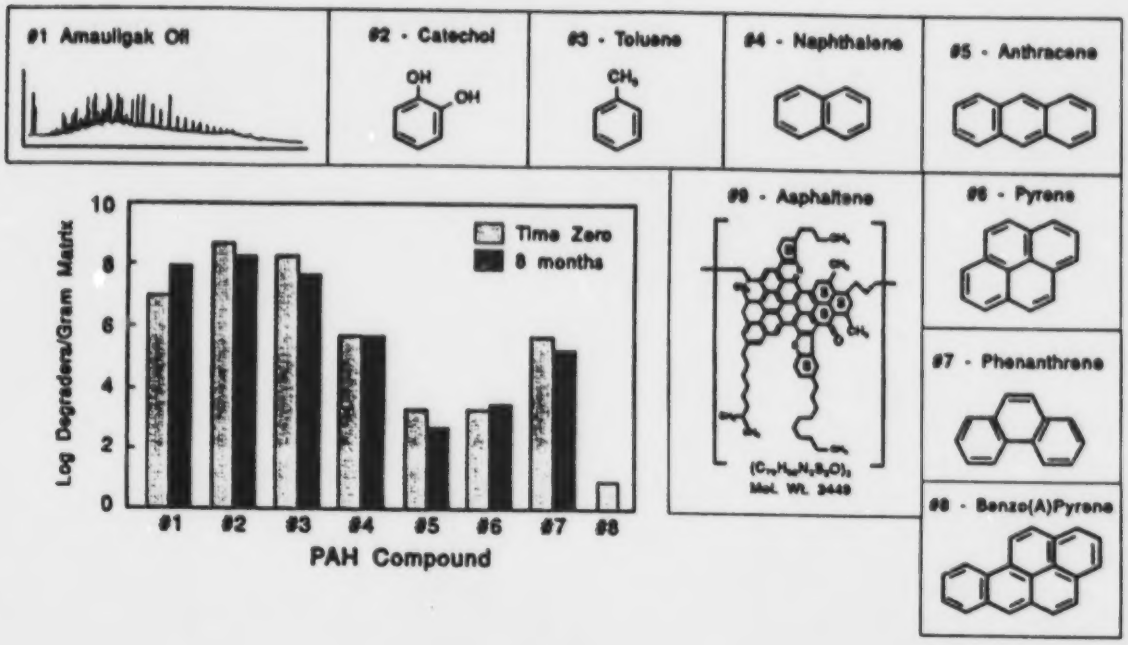


© 1991 NOVA HUSKY RESEARCH CORPORATION

FIGURE 3. LYSIMETER COLUMN APPARATUS AND PUMP IN OPERATION

© 1991 NOVA HUSKY RESEARCH CORPORATION

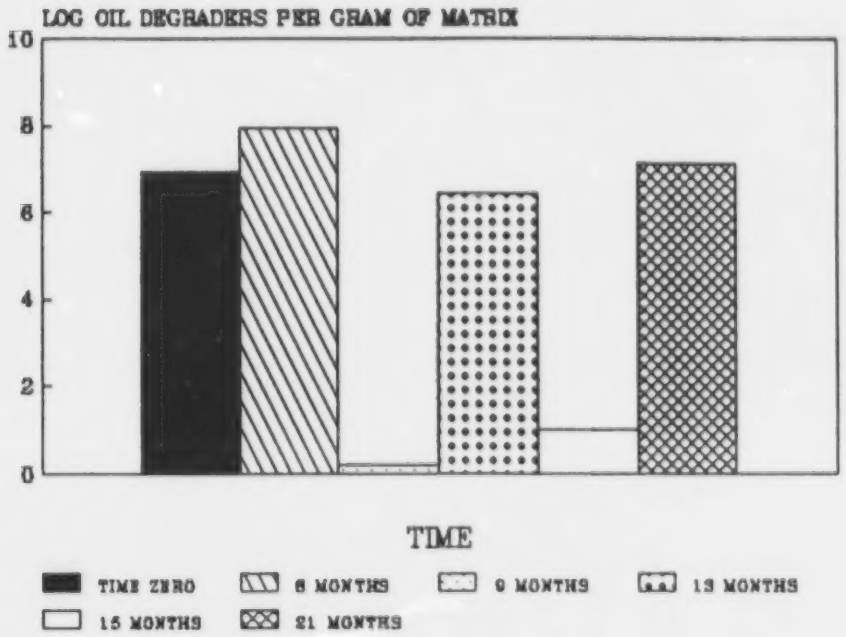
FIGURE 4. CHARACTERIZATION OF OIL DEGRADING ORGANISMS IN THE LLOYDMINSTER BIOREACTOR



No growth was obtained on asphaltene as a carbon source.

© 1991 NOVA HUSKY RESEARCH CORPORATION

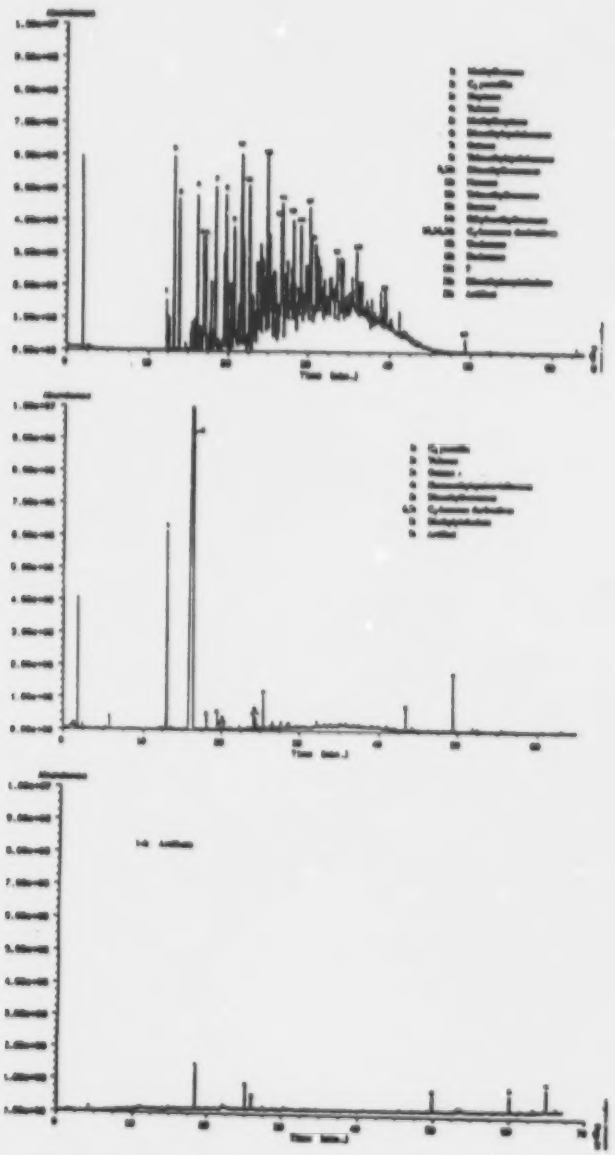
FIGURE 5. MICROBIAL NUMBERS IN THE BIOREACTOR



These organisms were capable of growing on Amauligak oil as a carbon source.

© 1991 NOVA HUSKY RESEARCH CORPORATION

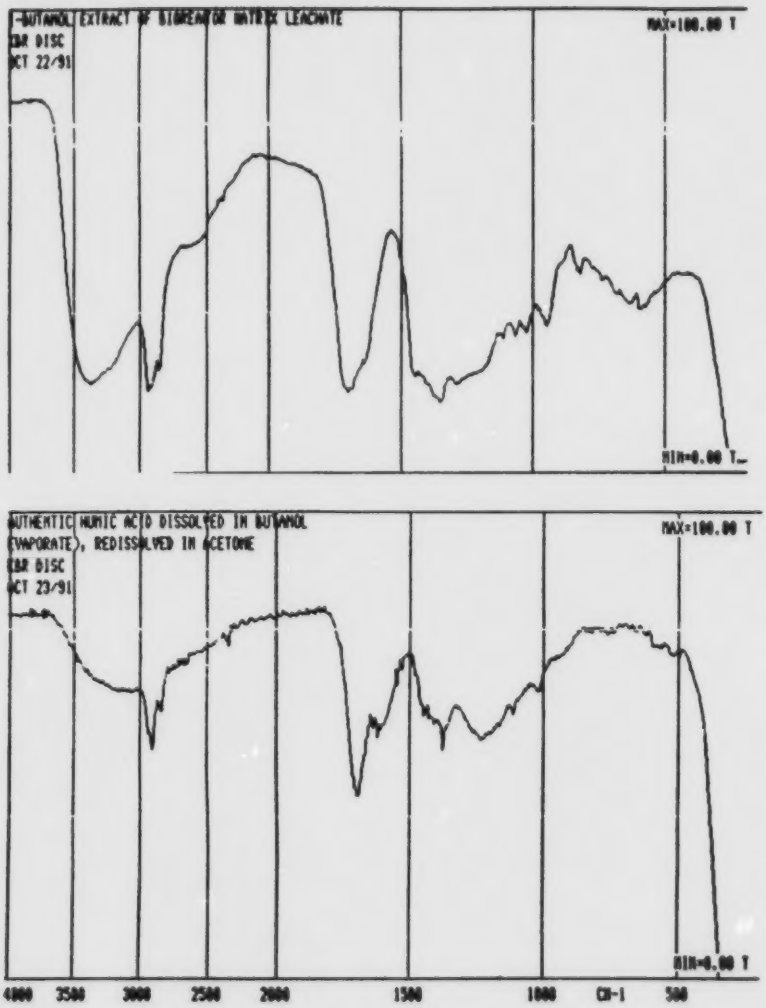
FIGURE 6. VOLATILES IN THE BIOREACTOR



The level of toluene in the bioreactor at zero time (upper panel) is compared to the level present at eight months (middle panel). Toluene disappeared at 12 months (lower panel)

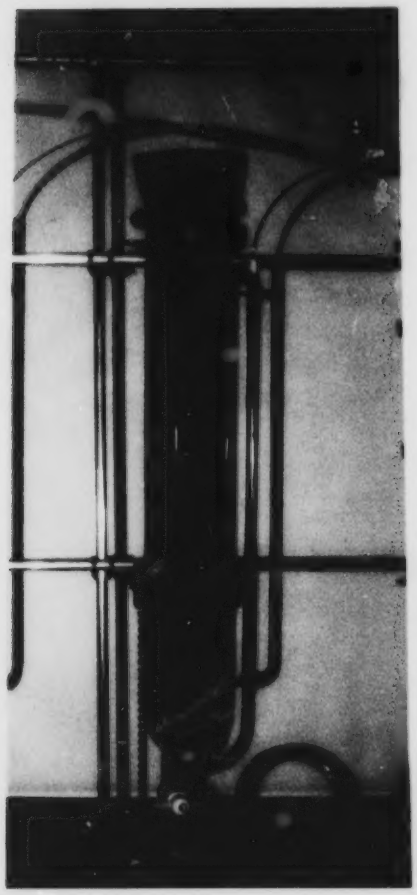
© 1991 NOVA HUSKY RESEARCH CORPORATION

FIGURE 7. **INFRA RED SPECTRUM OF THE BUTANOL EXTRACT OF THE BIOREACTOR LEACHATE (UPPER PANEL) COMPARED TO THAT OF AUTHENTIC HUMIC ACID (LOWER PANEL)**



© 1991 NOVA HUSKY RESEARCH CORPORATION

FIGURE 8. OIL SEPARATION FROM HAZORB IN LYSIMETER COLUMN

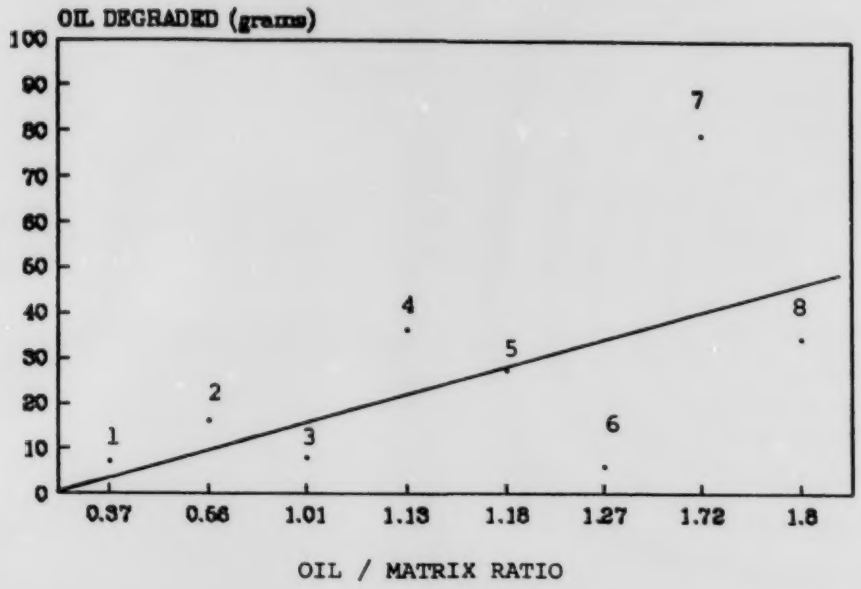


© 1991 NOVA HUSKY RESEARCH CORPORATION

FIGURE 9. BIOFILM RUNNING OUT OF LYSIMETER COLUMN

© 1991 NOVA HUSKY RESEARCH CORPORATION

FIGURE 10. COMPARISON OF THE AMOUNT OF OIL DEGRADED IN LYSIMETER COLUMNS AS A FUNCTION OF OIL: MATRIX RATIO



1 = Fuller's Earth

2,8 = Biosorb

3,4,6,7 = Oclansorb

5 = Reused Oclansorb

© 1991 NOVA HUSKY RESEARCH CORPORATION

APPENDICES

© 1991 NOVA HUSKY RESEARCH CORPORATION

APPENDIX 1

METHODS OF WATER ANALYSIS

© 1991 NOVA HUSKY RESEARCH CORPORATION

METHOD W-10

ANALYSIS OF ANION CONTENT IN WATER

A) REFERENCES:

1) ASTM D4327-84 Anions in Water by Ion Chromatography
2) EPA The Determination of Inorganic Anions in Water by Ion Chromatograph - Method 300.0
3) Dionex Ion Chromatography Cookbook

B) SCOPE:

This method is used in the analysis of various types of waters to separate and quantitatively detect chlorides, fluorides, nitrates, phosphates and sulphates, using the Dionex 2000i ion chromatograph. (Note #4)

C) SUMMARY:

The sample is injected into the sample port, where it passes through a prefilter (bed support) which removes any undissolved particles from getting on the chromatographic columns. The sample is then pushed by the eluent (aqueous $NaHCO_3$ & Na_2CO_3) (onto the neutral guard column) where unwanted organic molecules are removed. The next column that the sample travels through is an anion guard column which removes any large anions that may contaminate the actual separator column. (The neutral guard column and the anion guard column are expendable and can easily be replaced while the actual separator column is much more expensive to replace.) The partially separated sample then enters the separator column where the majority of anion separation occurs. Because each anion has a different affinity for the ion exchange resin sites it passes some anions stay in the stationary phase. longer than others before being displaced by the eluent. This produces bands of the same anion travelling together along the column. After the separator column the anions and eluent continue along to the suppressor, where the eluent exchanges its Na^+ for H^+. This increases the hydronium ion content forcing the equilibrium to favour H_2CO_3. Carbonic acid has a much lower conductivity than its individual ions ($H^+H^+CO_3^=$). This reduces the background noise (conductivity) so that the anion to be detected is the dominant ionic species. The anions are detected by a conductivity cell. As the conductivity created by each anion band is measured, a peak is produced by the conductivity

versus time plot. The concentration of each anion present is determined by peak height or area. The solution leaves the conductivity cell and enters a waste reservoir, and is then discarded.

D) **INTERFERENCES:**

1) The suppressor must be working to its full potential for ion exchange at all times. If it is not, the background noise (conductivity) will be higher than the anion conductivities. (i.e. peaks will be covered by baseline and never be seen or detected.)
2) The glassware used to make solutions, eluents and regenerant must be clean, along with clean syringes to prevent contamination from occurring. (See Cleaning Procedure for Trace Analysis)
3) If there are other ions in the sample, with the same retention times they may overlap with those anions being analyzed and cause false readings(i.e. organic acids (formate & acetate) elute at the same time as fluoride but have a much broader peak.
4) As the columns are used repeatedly over time, they begin to deteriorate due to contaminants building up on the ion exchange resin sites. This reduces the efficiency of your columns and therefore your analysis.
5) Air bubbles in the tubing, columns, pump, or conductivity cell will cause baseline upset.
6) Water dip occurs very close to F & Ce peaks - add concentrated eluent to sample and insure proper integration at peak shear water dip.

E) **SAFETY:**

1) Use normal laboratory safety procedures.
2) Rubber gloves, safety glasses and protective clothing must be worn when handling H_2SO_4.
3) Refer to Material Safety Data Sheets for detailed information on reagents.

F) **APPARATUS:**

1) Ion Chromatograph with a temperature compensated conductivity meter and a constant flow pump 2 - 5 ml/min.
2) A neutral guard column to remove unwanted organic molecules (NG1).
3) A separator guard column to protect separator column (AG4A).
4) A separator column to separate anions (AS4A).
5) A suppressor column to exchange sodium for hydrogen ions (AMMS).
6) Eluent and regenerant reservoirs.
7) A recorder, preferrably with an integrator.
8) Grade A volumetric flasks, and pipettes for dilutions.
9) Syringes.

G) **REAGENTS:**

1) Anion Regenerant: An 18 millimolar H_2SO_4 solution is required, add 2 ml of concentrated (36N) H_2SO_4 to four (4) litres of deionized water that has a resistance greater than 18 mega ohms. The absolute accuracy of the regenerant solution is not critical. A roughly calibrated plastic jug is sufficient for solution preparation.
2) Mixed Anion Eluent: A 1.8 millimolar (0.763 g/4L) Na_2CO_3 and 1.7 millimolar (0.571 g/4L) $NaHCO_3$ aqueous solution is required. All reagents used for the eluents must be high purity. The deionized water must also have a resistance greater than 18 mega ohms, and must be degassed by purging with helium for 10 minutes.
3) Anion Standards - (Stock Solutions): A 1000 mg/L stock solution of each anion (fluoride, chloride, phosphate, nitrate and sulphate) is made from high purity reagents that have been dried at 105°C and cooled in a dessicator. The standards are made by serial dilutions using the stock solutions and 18 mega ohm deionized water, ranging from detection limits to 10 mg/L. Weights must be corrected for reagent purity.

F^- from NaF = 2.2100 g/L
PO_4 = $NaH_2PO_4 \cdot 2H_2O$ = 1.64273 g/L
Cl^- from NaCl = 1.6485 g/L
NO_3^- from $NaNO_3$ = 1.3708 g/L
SO_4 = Na_2SO_4

H) **PROCEDURE:**

a) Start Up:

If on Cation Mode:

1) Start pump and begin flushing deionized water through the system for 5 minutes at 2 ml/m.
2) Shut off pump and switch over to Anions.
3) Turn on Anion eluent and continue start-up procedure.

If on Anion Mode:

1) The ion chromatograph should be assembled according to manufacturer's specifications.
2) Start pump and begin flushing eluent through the system (2 ml/min.).
3) Turn regenerant on so it has a flow of 2-3 ml/min.
4) Turn compressed air and conductivity meter on.
5) Set conductivity on a 30 microSeimen range.
6) The instrument should be left for about one (1) hour to pump eluent through the columns, suppressor and detector until the pressure and baseline has stabilized.
7) Once the instrument has been allowed to stabilize, turn the auto-offset on.
8) Run blank to check baseline and for contamination.

Anion	Standard (mg/L)	Mean (mg/L)	Standard Deviation (SD)	95% Confidence Level	Relative Standard Deviation (%,RSD)	Detection Limits mg/L
Fluoride	1.0	0.9857	0.00947	± 0.02	0.96	0.1
Chloride	2.0	2.0142	0.02015	± 0.05	1.00	0.1
Nitrates	3.0	2.9983	0.01614	± 0.04	0.54	0.2
Phosphates	3.0	2.9914	0.01641	± 0.04	0.55	0.1
Sulphates	3.0	3.0028	0.01707	± 0.04	0.57	0.2

Detection limits can be lowered by lowering microSiemen range to 3 µS and lowering standard concentrations.

L) **QUALITY CONTROL:**

1) Conductivity meter must be calibrated after every cleaning.
2) The anion calibration standards should be checked against each other and by using a certified standard monthly. (Note #5) The anion concentrations inthe standards may change due to evaporation; or contamination. The lids must always be kept on the standards to decrease the possibility of evaporation.
3) Deionized water must have a resistance greater than 18 mega ohms to be used for all standards, eluents, regenerant and dilutions.
4) The deionized water must be degassed by purging it with helium when mixing up the eluents.
5) All reagents used must be of high purity.

M) **REPORTING:**

a) **Significant Figures:**

1) Two (2) significant figures are reported.
2) When dealing with trace amounts of an anion, the Dionex 2000i is accurate to one (1) decimal point.

b) **Format:**

1) All results from the ion chromatograph are listed as mg/L.

N) **NOTES:**

1) The water is the first thing to come off the column and be detected. Water has a much lower conductivity than that of the eluent. A dip is made on the recorder paper when the water is detected by the condictivity meter. This sometimes causes integration problems if you have an integrator attached to your recorder. The water dip may be eliminated by adding concentrated eluent to all standards and samples.

2) To check if glassware is indeed clean after the cleaning procedure, place deionized water (with an 18 mega ohm resistance) in the container and let stand for a few minutes. Inject deionized water from glassware into the ion chromatograph. The ion chromatograph will detect if any contaminants are still present on the glassware.
3) The hands and fingers are the worst form of contamination to occur. Keep hands away from syringe tips, and hands out of standard and sample solutions.
4) This method can also be used for nitrites, sulfites, and thiosulfites but due to the instability of these products a reference standard is used.
   i.e. Nitrate for Nitrite
   Sulfate for Sulfite and Thiosulfite
5) Results should be within precision of the method (1% RSD).

REVISION DATE:

METHOD W13

pH OF WATER

A) **REFERENCES:**

1) Alberta Environment - Methods Manual for Chemical Analysis of Water and Wastes - METHOD NAQUADAT No. 1030IL
2) Operating Instructions PHM82 Standard pH Meter Radiometer

B) **SCOPE:**

This method is used for determining the pH of all types of water samples with pH 0 - 14.

C) **SUMMARY:**

Two electrodes, a glass electrode and a reference electrode (usually a saturated calomel) are used for pH measurement. The glass electrode has a glass membran which forms a partition between the liquid sample and an internal solution of constant pH. The potential developed between the glass electrode and the saturated calomel electrode is measured electrometrically.

pH is defined as the logarithm of the reciprocal of the hydrogen ion concentration (the hydrogen ion activity) in moles per liter.

D) **INTERFERENCES:**

1) High sodium concentrations at a pH above 10 corrections can be made according to a chart supplied by electrode manufacturer.
2) Oil and solids interfere with efficiency of probe - clean sample as much as possible.

E) **SAFETY:**

1) Routine safety equipment use is all that is required (eg. safety glasses, plastic gloves).

F) **APPARATUS:**

1) pH meter - PHM82 Radiometer
2) Glass electrode
3) Reference electrode (saturated calomel)
4) Stirring plate
5) Stirring bar
6) Beakers (100 ml)

G) REAGENTS:

1) Commercial standard pH buffer solutions - pH 4.0, 7.0, 10.0.
2) Saturated KCl solution.
3) Deionized water.

H) PROCEDURE: (Note #1)

a) CALIBRATION:

1) Set temperature compensator of the pH meter to room temperature.
2) Place pH 7.0 buffer solution in a beaker with a stirring rod, place on stirring plate and set sample stirring.
3) Place the electrodes in the solution being careful not to let the electrodes get hit with the stir bar.
4) Press the hold button off (light is off) and allow the pH to stabilize.
5) Use a combination of the sensitivity button and the buffer knob to adjust the pH reading to 7.00. Allow to stabilize.
6) To change the sample, press the hold button, turn off the stirrer and remove the electrodes from the solution.
7) Wash the electrodes with deionized water and dry with a soft tissue.
8) With the 4.00 or the 10.00 pH buffer solution repeat steps 2 to 7. (Note #2)
9) As a check determine the pH 7.0 buffer solution.

b) ANALYSIS:

1) Samples are to be kept cool and analyzed as soon as possible.
2) Place the water sample to evaluated in a beaker or paper cup together with a stirring bar and place on the stirring plate. Set the sample stirring.
3) Place the electrodes in the sample solution being careful not to let the electrodes get hit with the stir bar.
4) Press the hold button off (light is off) and allow the pH to stabilize.
5) Record the number observed.
6) Press the hold button on, turn off the stirrer and remove the electrodes from the sample.
7) Wash the electrodes with deionized water.
8) When the analyses are finished, clean the electrodes as per the cleaning procedure.
9) Store the calomel electrode in a pH 7.00 buffer solution. Store the glass electrode in a 4.00 to 7.00 ph buffer.

I) CLEANING:

1) Electrodes:
   a) CALOMEL ELECTRODE:
      i) Soak electrode in xylene or chloroform for 15 minutes.

ii) Rinse electrode with isopropyl alcohol or acetone.

iii) Push KCl electrolyte into the top of the electrode and watch for drops to form out of the bottom porous plug.

iv) If the porous plug is still dirty or you cannot get good readings when you try to calibrate, repeat steps i to iii.

v) If this still does not work soak in 1N HCl for 15 minutes, rinse with distilled water and squeeze a drop of KCl through the porous plug.

vi) If this still does not work soak in chromic acid for a maximum of 15 minutes, rinse with distilled water and squeeze a drop of KCl through the porous plug.

b) GLASS ELECTRODE:

i) Soak electrode in xylene or chloroform for 15 minutes.

ii) Rinse electrode with isopropyl alcohol or acetone.

iii) If the electrode still does not appear clean, soak in 1N HCl for up to 24 hours and rinse with distilled water.

iv) If the electrode is still not clean, soak for a maximum of 15 minutes in chromic acid and rinse with distilled water.

c) HACH ELECTRODE:

i) To clean, when electrode response becomes sluggish, immerse the electrode tip in 0.1N hydrochloric acid for 2 minutes, followed by immersing in 0.1N sodium hydroxide for 2 minutes, then immersion in 0.1N hydrochloric acid for another two minutes. Rinse with deionized water and soak in deionized water for at least 15 minutes.

ii) This electrode can be stored air-dry. It responds well when re-immersed in strong buffer.

iii) The electrolyte solution in the reference electrode (2.2N potassium chloride) may form crystals. This can be corrected by immersing the electrode in warm water (30°C).

d) All beakers and other glassware are to be washed with soap and water and rinsed with distilled water.

J) CALCULATIONS: 1) None.

K) PRECISION: 1) The meter is accurate to ±0.10 pH.

L) QUALITY CONTROL:

1) Analyze samples with known pH to check the calibration and accuracy of the instrument.

M) REPORTING:

a) Significant Figures:

1) Report to the second figure after the decimal.

b) Format: 1) Report as:

pH X.XX

N) NOTES:

1) The outlined method is for the electrode system designed by Radiometer. We also have an electrode system designed by Hach which consists of a dispensette for electrolyte solution and plastic electrode. This system only works for clean waters.
2) It is only necessary to use two buffer solutions to set the calibration. Whether you use 4.00 or 10.00 as your second, buffer is determined by the pH of the actual samples.

REVISION DATE:

METHOD W15

METALS BY ATOMIC ABSORPTION

A) **REFERENCES:**

1) Analytical Methods for Atomic Absorption Spectrophotometry, Perkin Elmer

B) **SCOPE:**

This method is applicable to the analysis of surface, waste, and produced waters and any materials which can be dissolved or converted by chemical processes to aqueous solutions where the metal contents are in the mg/L range.

C) **SUMMARY:**

An aqueous solution of a metal is aspirated into a burner fired by either an acetylene-air or acetylene-nitrous oxide mixture. A light beam, from a hollow cathode lamp of the metal being analyzed, is passed through the flame. The absorbance of the beam caused by the metal in the flame is detected and compared against a standard curve to yield the concentration.

D) **INTERFERENCES:**

1) Some metals are readily excited to emission which means the atoms cannot absorb light. Sodium chloride is added to such metal solutions to reduce this interference.
2) Some metals react strongly with other ions or with the oxygen in the flame to form very stable compounds or refractory oxides. These will not allow the metal to atomize in the flame. This effect is countered by adding lanthanum chloride to the solutions or by using the hotter acetylene-nitrous oxide flame.
3) Specific chemical interferences for each metal are described in the Standard Conditions Table, Table 1 (see Standard Conditions Section of the Operator's Manual for more details) along with techniques for handling each one.
4) Oil or sediment can block and foul aspirator tubes and nozzles. This is avoided by filtering the samples.

5) Flame absorbances and emissions may interfere with the absorption bands of some elements. Using an alternate wave length will avoid this situation.
6) Self-absorption causes non-linearity and usually occurs at high concentrations. Dilution of these strong solutions usually corrects this problem.
7) Matrix interferences result from the physical characteristics of the solvent (viscosity, high surface tension, combustible solvent). To overcome these problems the operator should use the same solvent in standards and samples. Dilute high TDS samples or use the method of standard addition where all else fails. (Note #1)
8) Background interferences caused by light scattering of particles or molecular absorbance can be avoided by using a hotter flame or by using the Centurium Arc Background Correction.

E) SAFETY:

1) Acetylene:
   a) Cylinders transported on their side should be stored upright for at least 24 hours before using. Failure to do so may cause acetone/acetylene to be drawn into the regulator and result in a violent explosion.
   b) The main cylinder valve should never be opened more than 1/3 to 1/2 turn to prevent acetone excaping from the cylinder during a catastrophic line failure. It also permits quicker shutdowns under these circumstances.
   c) Acetylene cylinders should never be drawn below 520 kpa (75 psi).
   d) The acetylene delivery pressure to the A.A. should never exceed 70 kpa (10 psi) as pure acetylene spontaneously dissociates at high pressure.
   e) For more information, see Appendix A.
2) When handling hot burner heads, insulated gloves should be used to prevent burns.
3) Before using the A.A., ensure the trap on the drain line is filled with water to prevent escape of gases through the drain container.
4) Ventilation fan must be used to remove toxic combustion gases or vented fuel gases.
5) Refer to the Material Safety Data Sheets for detailed information on reagents and fuel gases.

F) APPARATUS:

1) 3 - 10 ml dispensettes with 1 litre reservoir bottles.
2) 100 ml volumetric flasks (as required).
3) 500 ml volumetric flasks (as required).

4) 500 ml plastic bottles with caps (as required).

5) Selection of pipettes suitable for making accurate dilution.

6) Perkin-Elmer 3030 Atomic Absorption Spectrophotometer.

G) **REAGENTS:**

1) Concentrated nitric acid
2) Sodium chloride
3) Lanthanum chloride
4) Acetylene
5) Nitrous oxide
6) 1000 mg/L standard solutions

H) **PROCEDURE:**

a) **CALIBRATION:**

1) Prepare 3 calibration standard and 1 reference standard as per Table #2. (Note #2)
2) Turn on ventilation fan and instrument power.
3) Install the required burner head.
4) Open the main acetylene valve 1/3 to 1/2 turn.
5) Open the air valve and nitrous oxide valve (if required).
6) Set the appropriate fuel and oxidizer flow rates:

	FUEL	OXIDANT
Air/Acetylene	20	45
N_2O/Acetylene	33	33

7) Install or rotate the appropriate hollow cathode lamp into position.
8) Recall the appropriate program from the User Index. (Note #3)
9) Set the lamp current to the continuous operating valve stamped on the lamp.
10) Set the slit-width and wavelength as per the method on the monitor.
11) Set the instrument on Set-up mode, optimize the wavelength and lamp position (see Operator's Manual).
12) Light the burner and allow a minimum of 15 minutes for warm-up.
13) Aspirate the Sensitivity Check Standard and optimize the burner vertical, horizontal, and rotational controls and optimize the aspirator flowrate (see Operator's Manual).
14) Switch to an operating mode, aspirate a blank and set zero.
15) Starting with the lowest concentration, aspirate each of the calibration standards and press its calibration key. Re-zero between each standard.
16) Check the calibration by reading the reference standard. This should agree to within 4.0% of its known concentration.

b) ANALYSIS:

1) All samples, except silica (Note #4) should be preserved by acidifying with 1.0% by volume of concentrated nitric acid.
2) Re-zero the instrument using a blank.
3) Add any acids and reagents as listed in the Standard Conditions (Table 1) for the element in question.
4) Samples with oil or suspended solids require filtration before analysis.
5) Aspirate the sample and read the concentration from the monitor.
6) If the sample is too concentrated, make an accurate dilution using pipettes and volumetrics, re-treat with the appropriate reagents and repeat the analysis.
7) If the concentration is too low, the flow spoiler may be replaced with the impact bead for air/acetylene flames only. (Note #5)
8) After every 5 samples, run a calibration standard to ensure accuracy of calibration.

I) CLEANING:

1) Glassware:
   a) Normal laboratory procedure should be adequate.

2) Aspirator (Minor Cleaning):
   a) If the aspirator becomes clogged with oil or sediments it can frequently be cleared by passing a wire through the aspirator tubing and assembly. (Note #5)
   b) Re-check the calibration before continuing with analysis.

3) Aspirator (Major Cleaning):
   a) If the above fails to clear the problem, shut down the burner and dismantle the aspirator assembly.
   b) Wash the metal parts and tubing with solvent and/or soap and water.
   c) Use the cleaning wire to clear any debris from the tubing or needle.
   d) Re-assemble the aspirator (Figure #1).
   e) Re-light and re-warm the burner, adjust the aspirator and recalibrate before continuing the analysis.

4) Burner Heads:
   a) All burner cleaning requires shutting down of the burner. (Note #7).
   b) Carbon, salt and other deposits on the burner slot can be removed using the razor blade or scraper tool provided.
   c) More tenacious deposits can be removed by soaking the head in water and brushing with a bottle

brush and using the scrapers.

d) Burner heads are to be cleaned at the completion of each sample batch.

5) Premix Chamber:

a) After completion of each batch of samples the premix chamber should be flushed with distilled water to remove salt solutions and deposits.

b) If the walls are oily, the burner assembly should be dismantled, solvent washed, wiped clean and water rinsed. The unit is then re-assembled. (Figure #2)

J) CALCULATIONS: 1) $C = \frac{V \times A}{S}$

V = Final dilution volume, ml
S = Sample aliquot, ml
A = Instrument reading, mg/L
C = Original sample concentration, mg/L

K) PRECISION: 1) Duplicate results shall agree to within 5.0 % of each other.

L) QUALITY CONTROL:

1) Results which fail the precision criterion shall be repeated.
2) A calibration check shall be run after every fifth sample, utilizing the standard closest to the last sample analyzed.
3) Failure of the standard to fall within 4.0 % of its known value requires the operator to recalibrate and repeat the five previous analyses with another calibration check included.

M) REPORTING:

a) Significant Figures: (See Technical Section)

1) All results shall be reported to 3 significant figures.

b) Format: 1) The following format is recommended:

Metal, mg/L	XX.X
eg. Calcium, mg/L	1 230.

N) NOTES: 1) See the Operator's Manual for the method of standard additions. This approach is rarely used at this time and therefore does not warrant being published and is only included for completeness.

2) One of the four standards doubles as the Sensitivity Check.
3) See the Operator's Manual for selecting and initializing new user index programs.
4) Silica samples should never be acidized. Cool to 4.0°C and analyze within 7 days.
5) The use of the impact bead doubles the sensitivity of the element with air/acetylene flames. Use of the bead with N_2O/acetylene flames usually has no effect and therefore is not recommended.
6) This can be done while the instrument is operating, avoiding a shut-down and re-warming of the burner.
7) Exercise care in handling hot burners. Use insulated gloves and avoid contact with hot components in the burner compartment.

REVISION DATE:

METHOD W16

METALS BY EMISSION

A) REFERENCES:

1) Analytical Methods for Atomic Absorption Spectrophotometry, Perkin Elmer

B) SCOPE:

This method is applicable to the analysis of surface, waste, and produced waters and any materials which can be dissolved or converted by chemical processes to aqueous solutions where the metal contents are in the mg/L range.

C) SUMMARY:

An aqueous solution of a metal is aspirated into a burner fired by an air/acetylene mixture. The metal atoms are promoted to excited states and on returning to their ground state emit characteristic spectral bands of light. The amount of light emitted is detected and compared to a set of standards to determine the metal content of the sample.

D) INTERFERENCES:

1) Oil or sediment can block and foul aspirator tubes and nozzles. This is avoided by filtering the samples.
2) Flame absorbances and emissions from other elements may interfere with the emission bands of some elements. Using an alternate wave length will avoid this situation.
3) Self-absorption causes non linearity and usually occurs at high concentrations. Dilution of these strong solutions usually corrects this problem.
4) Matrix interferences result from the physical characteristics of the solvent (viscosity, high surface tension, combustible solvent). To overcome these problems the operator should use the same solvent in standards and samples, dilute high TDS samples or use the method of standard addition where all else fails. (Note #1)

4) Open the main acetylene valve 1/3 to 1/2 turn.
5) Open the air valve.
6) Set the fuel flowrate at 20 units and oxidizer flowarate at 45 units.
7) Recall the appropriate program from the User Index. (Note #2)
8) Set the slit-width and wavelength as per the method on the monitor.
9) Light the burner and allow a minimum of 15 minutes for warm-up.
10) Set the instrument on Set-up Mode and aspirate the most concentrated standard.
11) Optimize the wavelength setting, the burner vertical, horizontal and rotational settings, and the aspirator adjustment, resetting the gain as required. (See Operator's Manual).
12) Switch to an operating mode, aspirate a blank and set zero.
13) Starting with the lowest concentration, aspirate each of the calibration standards and press its calibration key. Re-zero between each standard.
14) Check the calibration by reading the reference standard. This should agree to within 5.0% of its known concentration.

b) ANALYSIS:

1) All samples should be preserved by acidifying with 1.0% by volume of concentrated nitric acid.
2) Re-zero the instrument using a blank.
3) Add any acids and reagents as listed in the Standard Conditions (Table 1) for the element in question.
4) Samples with oil or suspended solids require filtration before analysis.
5) Aspirate the sample and read the concentration from the monitor.
6) If the sample is too concentrated, make an accurate dilution using pipettes and volumetrics, re-treat with the appropriate reagents and repeat the analysis.
7) After every 5 samples, run a calibration standard to ensure accuracy of calibration.

I) CLEANING:

1) Glassware:
   a) Normal laboratory procedure should be adequate.

2) Aspirator (Minor Cleaning):
   a) If the aspirator becomes clogged with oil or sediments it can frequently be cleared by passing a wire through the aspirator tubing and assembly. (Note #3)
   b) Re-check the calibration before continuing with analysis.

3) Aspirator (Major Cleaning):
   a) If the above fails to clear the problem, shut down the burner and dismantle the aspirator assembly.
   b) Wash the metal parts and tubing with solvent and/or soap and water.
   c) Use the cleaning wire to clear any debris from the tubing or needle.
   d) Re-assemble the aspirator (Figure #1).
   e) Re-light and re-warm the burner, adjust the aspirator and recalibrate before continuing the analysis.

4) Burner Heads:
   a) All burner cleaning requires shutting down of the burner. (Note #4).
   b) Carbon, salt and other deposits on the burner slot can be removed using the razor blade or scraper tool provided.
   c) More tenacious deposits can be removed by soaking the head in water and brushing with a bottle brush and using the scrapers.
   d) Burner heads are to be cleaned at the completion of each sample batch.

5) Premix Chamber:
   a) After completion of each batch of samples the premix chamber should be flushed with distilled water to remove salt solutions and deposits.
   b) If the walls are oily, the burner assembly should be dismantled, solvent washed, wiped clean and water rinsed. The unit is then re-assembled. (Figure #2)

J) CALCULATIONS: 1) $C = \frac{V \times A}{S}$

V = Final dilution volume, ml
S = Sample aliquot, ml
A = Instrument reading, mg/L
C = Original sample concentration, mg/L

K) PRECISION: 1) Duplicate results shall agree to within 5.0 % of each other.

L) QUALITY CONTROL:

1) Results which fail the precision criterion shall be repeated.
2) A calibration check shall be run after every fifth sample, utilizing the standard closest to the last sample analyzed.
3) Failure of the standard to fall within 5.0 % of

its known value requires the operator to recalibrate and repeat the five previous analysis with another calibration check included.

M) REPORTING:

a) Significant Figures: (See Technical Section)

1) All results shall be reported to 3 significant figures.

b) Format: 1) The following format is recommended:

Metal, mg/L	XX.X
eg. Calcium, mg/L	1 230.

N) NOTES:

1) See the Operator's Manual for the method of standard additions. This approach is rarely used at this time and therefore does not warrant being published and is only included for completeness.
2) See the Operator's Manual for selecting and initializing new user index programs.
3) This can be done while the instrument is operating, avoiding a shut down and re-warming of the burner.
4) Exercise care in handling hot burners. Use insulated gloves and avoid contact with hot components in the burner compartment.

REVISION DATE: 1989-10-30

APPENDIX 2

DEAN STARK OIL EXTRACTION PROCEDURE

© 1991 NOVA HUSKY RESEARCH CORPORATION

SYNCRUDE
ANALYTICAL METHODS FOR OIL SAND AND BITUMEN PROCESSING

SYNCRUDE CANADA LIMITED
EDMONTON, ALBERTA, CANADA
August 1979

Determination of Bitumen, Water and Solids Content of Middlings and Tailings Samples (Classical)

Scope: This method determines the bitumen, water and solids content of middlings and tailings samples. Preferred sample sizes range from 250 to 600 g, although the method may be modified for smaller samples.

Summary: The sample is separated into bitumen, water and solids by refluxing with toluene in a solids extraction apparatus. Condensed solvent and co-distilled water are continuously separated in a trap. The water is drained from the lower portion of the trap while the solvent recycles through the extraction thimble to dissolve bitumen. When the extraction is complete, the clean solids retained in the thimble are dried and weighed. A density measurement is employed to determine the bitumen content of the extract. Water is determined by difference.

Safety Considerations:

1. Hydrochloric acid — highly toxic by inhalation. A strong irritant to eyes and skin.
2. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Apparatus, Reagents, Materials:

1. Condenser — an indented tube condenser having a water jacket at least 535 mm long with a 29/42 standard taper male joint at the base.
2. Water trap — constructed to continuously separate water and solvent. The trap portion, which is approximately 25 mm in diameter and 220 mm long, has a volume of about 130 mL. The lower end is fitted with a stopcock for removal of water while the upper section has a 29/42 standard taper female joint to accommodate the condenser. The downcomer has a 103/60 standard taper male joint for connection to the kettle and is perforated with 3 mm diameter holes below the ground glass.
3. Kettle — a heat-resistant glass vessel having a capacity of 2000 mL. The neck has a minimum length of 390 mm and includes a 103/60 standard taper female joint.
4. Extraction thimble — Whatman 85 x 200 mm cellulose thimble, single thickness.
5. Thimble basket — a corrosion-resistant basket to support the thimble. See Figure 1. Fabrication from 3 mm diameter nichrome wire using a silver solder bottom joint is suitable.
6. Solvent distributor — corrosion-resistant, as shown in Figure 2.
7. Heating mantle — 500 W, to accommodate 2000 mL kettle.

The assembled extraction apparatus is shown schematically in Figure 3. If samples are less than 100 g, then the extraction apparatus described in Method 2.7 is used with the exception that the lower end of the water trap is fitted with a drain cock. Volumes employed in the following procedure are then gauged accordingly.

8. Kimwipes — Type 1300.
9. Supply of 800 mL beakers.
10. Volumetric flasks — 250 and 1000 mL, Class A.
11. Syringe — 5 mL, glass, Luer-Lok tip.
12. Disposable filter assemblies — Millipore Millex filters, 0.45 µm, 25 mm diameter, catalogue no. SLHA 025 OS.
13. Densimeter — six place densimeter with constant temperature water bath with temperature control to ±0.01°C. The water bath is operated at 20°C.
14. Balances:
    Top loading balance to ±0.01 g. 1200 g capacity.
    Analytical balance.

15. Drying oven — forced draft, set at 120°C.
16. Desiccator.
17. Reagents:
    Hydrochloric acid, A.C.S. reagent grade.
    Toluene, A.C.S. reagent grade.
18. Distilled water.

Procedure: Sample Handling

1. Insert 3 Kimwipes into each of a quantity of thimbles. Place the thimbles into 800 mL beakers and weigh to the nearest 0.01 g.
2. Clean the outer walls of the sample container and lid. Weigh to the nearest 0.1 g. Carefully add 0.5 mL of concentrated hydrochloric acid to the sample. Then add approximately 100 mL of toluene and stir until all the bitumen adhering to the wall of the sample container is dissolved.
3. Remove the Kimwipes from the thimble, insert the thimble into a thimble basket and mount the basket by its support into the neck of a kettle. Add approximately 900 mL of toluene to the kettle by pouring it through the thimble.
4. Restir the sample and while it is still in motion transfer to the thimble. Wash the container with toluene to remove all the bitumen. Add the washings to the thimble. Transfer the bulk of the remaining solids by scraping with a spatula. Finally, rinse and transfer remaining solids with distilled water. Clean and dry the container and lid with the Kimwipes and place them in the thimble. Weigh the container and lid.

Extraction

5. Assemble the extraction apparatus as shown in Figure 3, ensure all joints are vapour tight, and begin refluxing. Drain and discard water from the trap when it nears the trap overflow. The extraction is complete when the level of water in the trap is constant and solvent dripping from the thimble is clear. Terminate the extraction and allow the apparatus to cool.

Calibration of Densimeter

6. Prepare a series of standard solutions of middlings and tailings bitumen in toluene covering the range 0.3 - 12 g/250 mL. (a)
7. Filter the standards through a 0.45 μm filter and determine the density of the solutions to six places.
8. Prepare a calibration curve by plotting the density of the standards versus the bitumen concentration in grams of bitumen per 250 mL. Calculate the slope and intercept of the plot using a linear least square regression. Coefficients of determination better than 0.999 are expected. The calibration does not have to be repeated daily, but several points on the calibration curve should be checked periodically to confirm the calibration.

Bitumen Determination

9. Disassemble the extraction apparatus and pour the bitumen/toluene extract into a 1000 mL volumetric flask and dilute to volume with toluene. Filter several millilitres of the solution through a 0.45 μm filter and determine its density to six decimal places. Ensure that the measured density falls within the range of the calibration.

Solids Determination

10. Remove the thimble from the extraction apparatus, place it in its beaker and dry for 12 hours at 120°C. Cool and reweigh.

Calculations: The bitumen, water and solids contents of the sample are given by:

$$\% \text{ Bitumen} = \frac{B}{W} \times 100$$

$$\% \text{ Solids} = \frac{S}{W} \times 100$$

$$\% \text{ Water} = 100 - (\text{wt \% Bitumen} + \text{wt \% Solids})$$

where: W = weight of sample, g
S = weight of solids recovered in thimble, g

$$B = \frac{\text{Sample Density} - \text{Calibration Intercept}}{\text{Calibration Slope}} \times 4$$

= weight of bitumen in sample, g

Precision: Data tabulated below indicates typical precision values associated with the bitumen water and solids analysis of middlings and tailings samples. Estimates reflecting the repeatability of a middlings analysis were determined on 37 replicate subsamples prepared by Method 1.6 and analyzed using the small extractor assemblies. Precision values for primary and secondary tailings were evaluated from 10 replicate samples obtained in rapid succession from pilot plant process streams and analyzed using large extractor assemblies. All data includes errors due to sampling.

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Middlings			
Bitumen	7.32	±0.15	2.05%
Water	75.91	±0.42	0.55%
Solids	16.77	±0.38	2.27%
Primary Tailings			
Bitumen	0.87	±0.06	6.90%
Water	35.01	±1.47	4.20%
Solids	64.12	±1.48	2.31%
Secondary Tailings			
Bitumen	0.44	±0.02	4.55%
Water	79.98	±1.71	2.14%
Solids	19.58	±1.71	8.73%

Comments:

a. The bitumen for the standard solutions is prepared by extracting a large number of middlings and tailings samples on a solids extraction apparatus, removing non-filtered solids by centrifuging, removing toluene by evaporation, and determining the residual toluene content by the procedure described in Method 2.7.

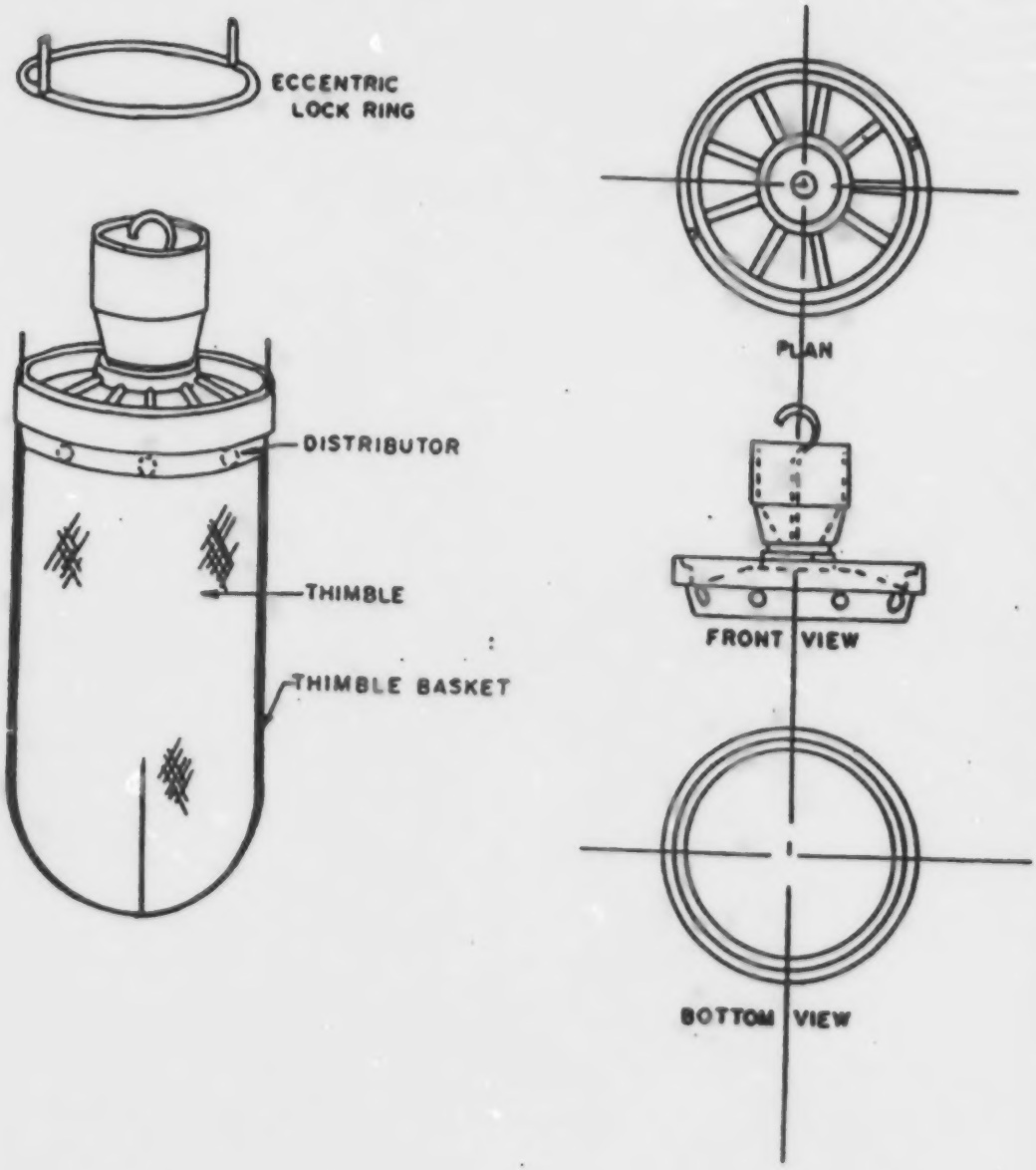


FIGURE 2: THIMBLE ASSEMBLY AND SOLVENT DISTRIBUTOR

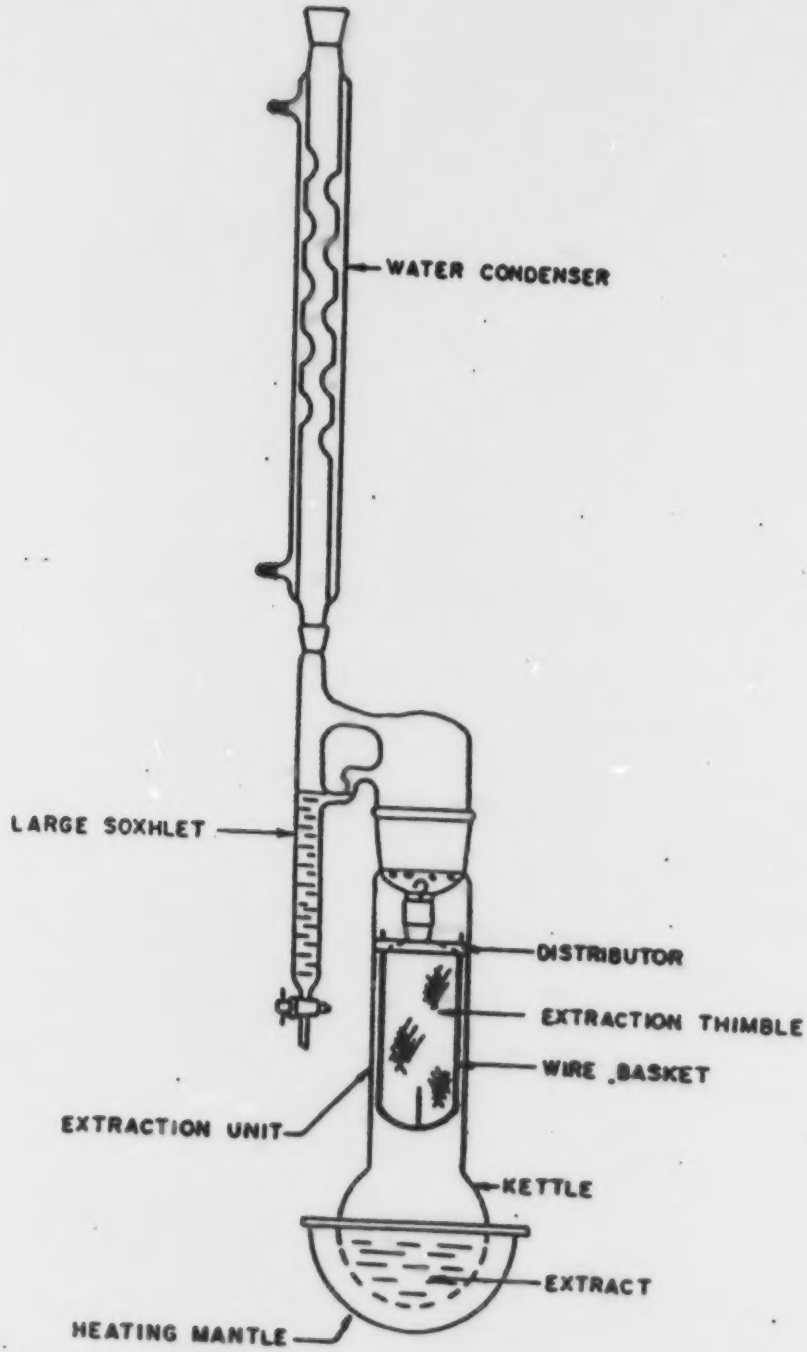


FIGURE 3: EXTRACTION APPARATUS

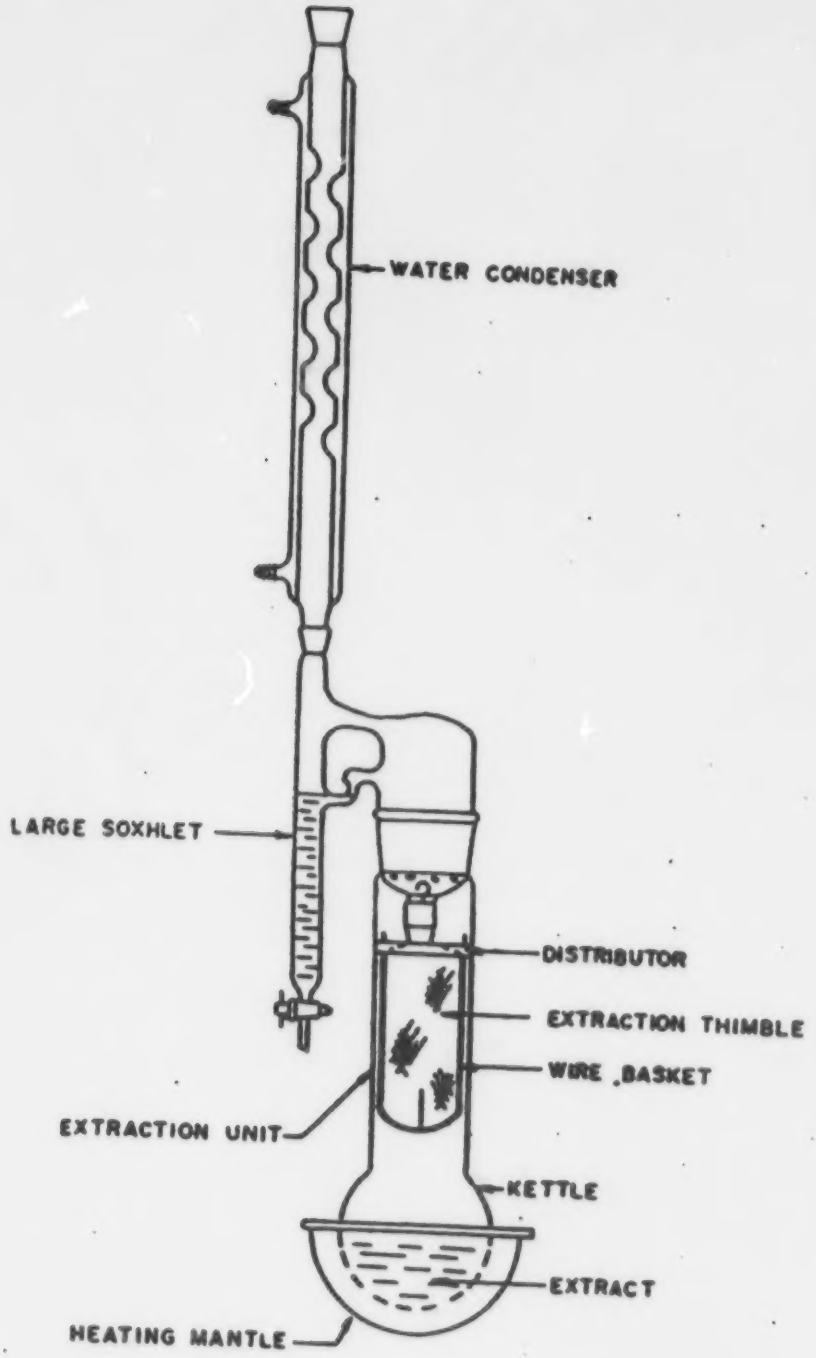


FIGURE 3: EXTRACTION APPARATUS

APPENDIX 3

FLAMMABILITY TEST METHOD

© 1991 NOVA HUSKY RESEARCH CORPORATION

SCHEDULE IV

(Sections 37 and 38)

METHODS OF TESTING FOR FLASH POINT

1. The method of testing for the flash point of

(*a*) a liquid, other than a liquid referred to in paragraph (*c*) or (*d*), having a viscosity of less than 5.8 mm²/s (45 Saybolt Universal Seconds) at 37.8°C (100°F) is the *Standard Test Method for Flash Point by Tag Closed Tester* ASTM D56-82, dated August 27, 1982, or the appropriate test in the *Standard Test Methods for Flash Point by Setaflash Closed Tester*, ASTM D3828-81, dated August 28, 1981;

(*b*) a liquid, other than a liquid referred to in paragraph (*c*) or (*d*), having a viscosity of 5.8 mm²/s (45 Saybolt Universal Seconds) or more at 37.8°C (100°F), is the appropriate test in the *Standard Test Methods for Flash Point by Pensky-Martens Closed Tester*, ASTM D93-80, dated August 29, 1980;

(*c*) an aviation turbine fuel is the appropriate test in the *Standard Test Methods for Flash Point by Setaflash Closed Tester*, ASTM D3828-81, dated August 28, 1981; and

(*d*) a paint, enamel, lacquer, varnish or similar liquid that has a flash point between 0°C (32°F) and 110°C (230°F) and a viscosity of less than 15,000 mm²/s at 25°C (77°F) determined in accordance with the *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)*, ASTM D445-83, dated October 28, 1983, is the appropriate test in the *Standard Test Methods for Flash Point of Liquids by Setaflash Closed-Cup Apparatus*, ASTM D3278-82, dated August 28, 1981.

ANNEXE IV

(articles 37 et 38)

MÉTHODES DE DÉTERMINATION DU POINT D'ÉCLAIR

1. La méthode de détermination du point d'éclair est :

a) dans le cas d'un liquide dont la viscosité à 37,8 °C (100 °F) est inférieure à 5,8 mm²/s (45 secondes universelles Saybolt) et qui n'est pas visé aux alinéas *c*) ou *d*), la méthode décrite dans la norme D56-82 de l'ASTM intitulée *Standard Test Method for Flash Point by Tag Closed Tester*, en date du 27 août 1982, ou la méthode décrite dans la norme D3828-81 de l'ASTM intitulée *Standard Test Methods for Flash Point by Setaflash Closed Tester*, en date du 28 août 1981;

b) dans le cas d'un liquide dont la viscosité à 37,8 °C (100 °F) est égale ou supérieure à 5,8 mm²/s (45 secondes universelles Saybolt) et qui n'est pas visé aux alinéas *c*) ou *d*), la méthode décrite dans la norme D93-80 de l'ASTM intitulée *Standard Test Methods for Flash Point by Pensky-Martens Closed Tester*, en date du 29 août 1980;

c) dans le cas d'un carburant d'aviation pour moteur à turbine, la méthode décrite dans la norme D3828-81 de l'ASTM intitulée *Standard Test Methods for Flash Point by Setaflash Closed Tester*, en date du 28 août 1981;

d) dans le cas de peinture, d'émail, de laque, de vernis ou d'un liquide similaire dont le point d'éclair se situe entre 0°C (32 °F) et 110 °C (230 °F) et dont la viscosité à 25 °C (77 °F) est inférieure à 15 000 mm²/s, déterminée selon la méthode D445-83 de l'ASTM intitulée *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)*, en date du 28 octobre 1983, la méthode décrite dans la norme D3278-82 de l'ASTM intitulée *Standard Test Methods for Flash Point of Liquids by Setaflash Closed-Cup Apparatus*, en date du 28 août 1981.

SCHEDULE V

(Paragraph 39(c))

METHOD OF TESTING FOR DETERMINING FLAMMABLE SOLIDS THAT IGNITE READILY

Preparation of Samples

1. For granules, powders and pastes, pack the sample into a flat, rectangular metal boat with inner dimensions 15.24 cm (6 in.) long and 0.63 cm (0.25 in.) deep.

2. For rigid and pliable solids, measure the dimensions of the sample and support it by means of metal ringstands, clamps, rings or other suitable devices as needed, so that the major axis

ANNEXE V

(alinéa 39c))

MÉTHODES D'ESSAI POUR LA DÉTERMINATION DES SOLIDES FACILEMENT INFLAMMABLES

Préparation des échantillons

1. Pour les granulés, les poudres et les pâtes, mettre l'échantillon, en le tassant bien, dans une nacelle métallique rectangulaire et plate ayant les dimensions intérieures suivantes : 15,24 cm (6 po) de longueur et 0,63 cm (0,25 po) de profondeur.

2. Pour les solides rigides ou souples, déterminer les dimensions de l'échantillon et le suspendre au moyen d'un support

is oriented horizontally and the maximum surface is freely exposed to the atmosphere.

Procedure

3. (1) Place the prepared sample in a draft-free area that can be ventilated and cleared after each test.

(2) The temperature of the sample at the time of testing shall be between 19.8°C (68°F) and 29.7°C (86°F).

(3) Hold a burning paraffin candle whose diameter is at least 2.54 cm (1 in.), so that the flame is in contact with the surface of the sample at the end of its major axis for five seconds or until the sample ignites, whichever is less, and remove the candle.

(4) Using a stopwatch, determine the length of time of combustion with self-sustained flame (the time not to exceed 60 seconds).

(5) Extinguish the flame with a CO_2 or similar non-destructive-type fire extinguisher.

(6) Measure the dimensions of the burnt area and calculate the rate of burning along the major axis of the sample in centimetres or inches per second.

SCHEDULE VI

(Section 40)

TEST FOR DETERMINING THE FLASHBACK AND THE LENGTH OF THE FLAME PROJECTION OF PRODUCTS, MATERIALS AND SUBSTANCES PACKAGED IN AEROSOL CONTAINERS

Application

1. This test is for use in determining any flashback and the length of the flame projection of any product, material or substance packaged in an aerosol container.

Apparatus

2. The following apparatus shall be used in carrying out this test:

(*a*) a flammability tester, illustrated in the figure, that

(i) is designed so that the aerosol container can be secured in place by means of a device, such as a three-pronged clamp affixed to a ring stand, in such a manner that the discharge from the container is in the horizontal plane,

(ii) may include a device by which the valve of any aerosol container can be activated by remote control such as a side-pull, caliper-type bicycle hand brake,

(iii) has a vertically mounted burner

universel, de pinces, d'anneaux ou d'autres dispositifs appropriés de façon que l'axe principal de l'échantillon soit à l'horizontale et que la plus grande surface possible de l'échantillon soit exposée à l'air.

Méthode

3. (1) Placer l'échantillon préparé dans un endroit qui est à l'abri des courants d'air et qui peut être ventilé et nettoyé après chaque essai.

(2) S'assurer que la température de l'échantillon au moment de l'essai se situe entre 19,8 °C (68 °F) et 29,7 °C (86 °F).

(3) Tenir la flamme d'une bougie en paraffine de 2,54 cm (1 po) de diamètre en contact avec la surface de l'échantillon, à l'extrémité de son axe principal, pendant cinq secondes ou jusqu'à ce que l'échantillon s'enflamme, s'il s'enflamme en moins de cinq secondes. Retirer la bougie.

(4) À l'aide d'un chronomètre, déterminer le temps de combustion après retrait de la source d'allumage. Ne pas laisser brûler plus de 60 secondes.

(5) Éteindre la flamme en utilisant du CO_2 ou un agent extincteur non destructif de type semblable.

(6) Déterminer les dimensions de la surface brûlée et calculer le taux de combustion le long de l'axe principal de l'échantillon, en centimètres ou en pouces par seconde.

ANNEXE VI

(article 40)

ESSAI POUR DÉTERMINER LE RETOUR DE FLAMME AINSI QUE LA LONGUEUR DE LA PROJECTION DE LA FLAMME DES PRODUITS DES MATIÈRES OU SUBSTANCES EMBALLÉS DANS DES CONTENANTS AÉROSOLS

Objet

1. Le présent essai a pour objet de déterminer le retour de flamme et la longueur de la projection de la flamme d'un produit, d'une matière ou d'une substance emballé dans un contenant aérosol.

Matériel

2. Le matériel suivant est nécessaire à l'essai :

a) un dispositif vérificateur d'inflammabilité, tel qu'il est illustré à la figure, qui présente les caractéristiques suivantes :

(i) il est conçu de façon à pouvoir tenir en place le contenant aérosol au moyen d'un dispositif de fixation tel une pince à trois doigts fixée sur un support universel, de sorte que le jet en soit expulsé horizontalement,

(ii) il peut comprendre un dispositif permettant d'actionner à distance la soupape du contenant par un moyen

APPENDIX 4

INFORMATION ON SUPERPHOSPHATE

© 1991 NOVA HUSKY RESEARCH CORPORATION

SAMPLE ENCLOSED AS PER REQUEST OF DAVID LOWERY LLOYDMINSTER

Regards Alan Dagl

ENGRO

Product Information

ENGRO 12-51-0-2
(MONOAMMONIUM PHOSPHATE)

CHEMICAL ANALYSIS — % BY WEIGHT	MIN.	TYPICAL
NITROGEN:		
TOTAL AS NITROGEN	12.0	
AMMONIA-WATER SOLUBLE AS NITROGEN	12.0	
PHOSPHORIC ACID AS P_2O_5:		
TOTAL AVAILABLE	51.0	
WATER SOLUBLE		43.3
CITRATE SOLUBLE		7.7
CITRATE INSOLUBLE		0.1
SULPHUR — AVAILABLE (WATER SOLUBLE SULPHATE)		2.0
MOISTURE		1.0
ACIDITY — pH OF 10% SOLUTION		3.8
PHYSICAL ANALYSIS		
ANGLE OF REPOSE (DEGREES)		30
BULK DENSITY (kg PER m^3)		
LOOSE		929
TAPPED		961
SIZE GUIDE NUMBER (SGN)		250

CONTENT

12% Water soluble nitrogen for healthy colour, fast growth, improved quality, yield and protein.

51% Phosphate for early root formation, fast start, good seed formation and to hasten maturity.

2% Readily available sulphate sulphur (SO_4) for higher yields and protein content; increased nitrogen efficiency, nodule formation of legumes.

BENEFITS

- Engro 12-51-0-2 is comprised of nitrogen and phosphate with sulphur as an extra bonus. It's uniform, free flowing granules store well and flow readily through fertilizer application equipment. Every granule of 12-51-0-2 is water soluble and ready to work as soon as it comes in contact with soil moisture.
- Engro 12-51-0-2 increases winter hardiness of fall sown crops; increases disease resistance; and increases the nutritional value of forage crops.

ESSO FARM-TEK™ RECOMMENDATIONS

Engro 12-51-0-2 is recommended for cereal grains, canola, legumes and grasses.

- Cereal Grain and Canola: Engro 12-51-0-2 drilled in gives cereals, grains and canola a fast start. Helps promote rapid root growth. Broadcast or band in additional nitrogen and potash as needed.
- Legumes and grasses: Broadcast Engro 12-51-0-2 for improving your stands of legumes and grasses.

ENGRO 12-51-0-2

PHOSPHORUS (P_2O_5) RATE
(lb/ac)

	MANITOBA	SASKATCHEWAN			ALBERTA		
CROP	BLACK	BROWN/ DK BROWN	BLACK	GREY WOODED	BROWN/ DK BROWN	BLACK	GREY WOODED
CEREALS	27 - 40	20 - 35	20 - 35	20 - 35	10 - 35	15 - 35	15 - 40
OILSEEDS*							
CANOLA/ MUSTARD	27 - 40	15 - 35	15 - 35	15 - 35	10 - 20	15 - 25	15 - 35
FORAGE							
GRASSES	27 - 45	0 - 20	0 - 40	0 - 40	0 - 15	0 - 30	0 - 40
LEGUMES	40 - 75	20 - 30	30 - 40	30 - 40	0 - 35	0 - 50	0 - 60

*No more than 18 lb/ac P_2O_5 should be placed with the seed. Contact your local Agricultural Representative for maximum seed placed rates for other crops.

Department of Agriculture; Manitoba, Saskatchewan and Alberta

PHOSPHORUS (P_2O_5) USED BY CROPS
(lb/ac)

CROP YIELD	WHEAT (40 bu/ac)	BARLEY (60 bu/ac)	OATS (80 bu/ac)	CANOLA (35 bu/ac)	GRASS/HAY (3 tons/ac)	ALFALFA (4 tons/ac)
SEED	24	22	21	32		
STRAW	5	8	13	14		
TOTAL	29	30	34	46	30	40

Western Canada Fertilizer Association

PHOSPHORUS DEFICIENCY SYMPTOMS

- Slow growth; plants respond poorly to other applied nutrients
- Purpling of lower leaves and stems
- Dark green coloration with tips of leaves dying
- Delayed maturity
- Poor seed development

Older leaves are usually first to show phosphorus deficiency symptoms since phosphorus is mobile in the plant.

ESSO PETROLEUM CANADA
EDMONTON, ALBERTA

Esso
Imperial Oil

APPENDIX 5

LEACHATE TEST CGSB-164-1MP

© 1991 NOVA HUSKY RESEARCH CORPORATION

Canadian General Standards Board CGSB

Office des normes générales du Canada ONGC

THE UNIVERSITY OF CALGARY
LIBRARY
APR 15 1987
GOVT. PUBS.

Leachate Extraction Procedure

This provisional standard sets out the requirements for determining the leachate extraction from solid waste materials

164-GP-1MP
February 1987

CA1
SA112
164-001

Canada

The CANADIAN GENERAL STANDARDS BOARD (CGSB), under whose auspices this standard has been developed is a government agency within the Federal Department of Supply and Services. The CGSB is engaged in the production of voluntary standards in a wide range of subject areas through the media of standards committees and the consensus process. The standards committees are composed of representatives of relevant interests including producers, consumers and other users, retailers, governments, educational institutions, technical, professional and trade societies, and research and testing organizations. Any given standard is developed on the consensus of views expressed by such representatives. The Minister's Advisory Council on CGSB reviews the results of the consensus process.

The CGSB has been accredited by the Standards Council of Canada as a national standards-writing organization. The standards that it develops and offers as National Standards of Canada conform to the criteria and procedures established for this purpose by the Standards Council of Canada. In addition to standards it publishes as national standards, the CGSB produces standards to meet particular needs, in response to requests from a variety of sources in both the public and private sectors. Both CGSB standards and national standards developed by the CGSB are developed in conformance with the policies described in the Policy Manual for the Development and Maintenance of Standards by CGSB.

CGSB standards are subject to review and revision at any time, so as to ensure that they keep abreast of technological progress. Suggestions for their improvement, which are always welcome, should be brought to the notice of the standards committees concerned. Changes to standards are issued either as separate amendment sheets or in new editions of standards.

An up-to-date listing of CGSB standards, including details on latest issues and amendments, and ordering instructions, will be found in the Catalogue of Standards and Qualified Products Lists which is published annually and is available without charge upon request.

Although the intended primary application of this standard is stated in its Scope, it is important to note that it remains the responsibility of the users of the standard to judge its suitability for their particular purpose.

Many tests required by CGSB standards are inherently hazardous. The CGSB neither assumes nor accepts any responsibility for any injury or damage that may occur during or as the result of tests, wherever performed.

The CGSB takes no position respecting the validity of any patent rights asserted with any item connected with this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights are entirely their own responsibility.

Further information on the CGSB and its services and standards may be obtained from:

The Secretary
Canadian General Standards Board
Ottawa, Canada
K1A 1G6

La présente norme a été élaborée sous les auspices de l'OFFICE DES NORMES GÉNÉRALES DU CANADA (ONGC), qui est un organisme fédéral relevant du ministère des Approvisionnements et Services. L'ONGC participe à la production de normes facultatives dans une gamme étendue de domaines, par l'entremise de ses comités des normes qui se prononcent par consensus. Les comités des normes sont composés de représentants des groupes intéressés aux normes à l'étude, notamment les fabricants, les consommateurs et autres utilisateurs, les détaillants, les gouvernements, les institutions d'enseignement, les associations techniques, professionnelles et commerciales ainsi que les organismes de recherche et d'essai. Chaque norme est élaborée avec l'accord de tous les représentants. Le Conseil consultatif du Ministre pour l'ONGC passe en revue les décisions prises par consensus.

Le Conseil canadien des normes a conféré à l'ONGC le titre d'organisme rédacteur de normes nationales. En conséquence, les normes que l'Office élabore et soumet à titre de Normes nationales du Canada se conforment aux critères et procédures établis à cette fin par le Conseil canadien des normes. Outre la publication de normes nationales, l'ONGC rédige également des normes visant des besoins particuliers, à la demande de plusieurs organismes tant du secteur privé que du secteur public. Les normes de l'ONGC et les normes nationales établies par cet organisme sont conformes aux politiques énoncées dans le Manuel des politiques d'élaboration et de mise à jour des normes de l'ONGC.

Étant donné l'évolution technique, les normes de l'ONGC font l'objet de révisions périodiques. Toutes les suggestions susceptibles d'en améliorer la teneur sont accueillies avec grand intérêt et portées à l'attention des comités des normes concernés. Les changements apportés aux normes font l'objet de modificatifs distincts ou sont incorporés dans les nouvelles éditions des normes.

Une liste à jour des normes de l'ONGC comprenant des renseignements sur les normes récentes et les derniers modificatifs parus, et sur la façon de se les procurer figure au Catalogue des normes et des listes des produits homologués publié chaque année. Cette publication peut également être obtenue sur demande, sans frais.

Même si l'objet de la présente norme précise l'application première que l'on peut en faire, il faut cependant remarquer qu'il incombe à l'utilisateur, au tout premier chef, de décider si la norme peut servir aux fins qu'il envisage.

Plusieurs des tests requis aux termes des normes de l'ONGC sont dangereux. L'ONGC n'assume ni n'accepte aucune responsabilité pour les blessures ou les dommages qui pourraient survenir pendant les essais, peu importe l'endroit où ceux-ci sont effectués.

L'ONGC ne se prononce pas quant à la validité de la propriété industrielle de chaque article assujetti à la présente norme. Les utilisateurs de la norme sont informés de façon personnelle qu'il leur revient entièrement de déterminer la validité de la propriété industrielle.

Pour de plus amples renseignements sur l'ONGC, ses services et les normes en général, prière de communiquer avec:

Le Secrétaire
Office des normes générales du Canada
Ottawa, Canada
K1A 1G6

Canadian General Standards Board
Office des normes générales du Canada

LEACHATE EXTRACTION PROCEDURE

This provisional standards has been published to meet an urgent requirement of the Ministry of Transport. It has not been approved by a technical committee nor ratified by the Minister's Advisory Council on CGSB.

It is intended that this standard will be formally approved and published as a bilingual National Standard of Canada in the near future.

164-GP-1MP
February 1987

PUBLISHED BY CANADIAN GENERAL STANDARDS BOARD, OTTAWA, CANADA K1A 1G6

©Minister of Supply and Services Canada — 1987

No part of this publication may be reproduced in any form without the prior permission of the publisher.

PUBLIÉE PAR L'OFFICE DES NORMES GÉNÉRALES DU CANADA, OTTAWA, CANADA K1A 1G6

©Ministre des Approvisionnements et Services Canada — 1987

Aucune partie de cette publication ne peut être reproduite d'aucune manière sans la permission préalable de l'éditeur.

CANADIAN GENERAL STANDARD BOARD

LEACHATE EXTRACTION PROCEDURE

1. SCOPE

1.1 This standard sets out the requirements for determining the leachate extraction from solid waste materials

2. APPLICABLE PUBLICATIONS

The following publications are applicable to this standard:

2.1 United States Environmental Protection Agency

EPA SW-846 Test Methods For Evaluating Solid Waste, September 1986

2.2 American Society for Testing and Materials (ASTM)

D1193 Standard Specification for Reagent Water

2.3 Reference to the above publications is to the issues in effect as of the date of this standard, unless otherwise specified. For the source of these publications, see the Notes section.

3. APPARATUS

3.1 Sieve, 9.5 mm mesh opening, stainless steel or plastic material.

3.2 Stainless steel filtration unit, 142 mm diameter, minimum 1L capacity, capable of sustaining a pressure of 500 kPa, applied to the solution to be filtered.

3.3 Membrane filter, 142 mm diameter, 0.45 µm diameter pore size, made of synthetic organic material such as teflon, cellulose acetate, cellulose nitrate, nylon or polycarbonate and which is compatible with the leachate to be filtered. Teflon is recommended for organic constitutents.

3.4 Glass fibre prefilter, 124 mm diameter, 3 µm to 12 µm pore size range.

3.5 Vacuum filtration unit, 90 mm diameter.

3.6 Membrane filter 90 mm diameter, 0.45 µm diameter pore size, made of synthetic organic material such as teflon, cellulose acetate, cellulose nitrate, nylon or polycarbonate and which is compatible with the leachate to be filtered. Teflon is recommended for organic constitutents.

3.7 Glass fibre filter 70 mm diameter, 3 µm to 12 µm pore size range.

3.8 Solid waste rotary extractor - a device that rotates the bottles end over end about a central axis through 360 °, with a speed of 10 rpm. The dimensions of the box will depend on the needs of each laboratory. See Figure 1.

3.9 Structural Integrity Tester with a 31.8 mm diameter hammer weighing 0.33 kilogram and having a free fall of 152.4 mm. See Figure 2.

3.10 pH meter, with a readability of 0.01 pH unit and accuracy of ± 0.1 pH units.

3.11 Cylindrical bottles, wide mouth, 1250 mL capacity, polyethylene or glass with lined cap for inorganic constituents; glass with Teflon-lined cap or Teflon bottles for organic constituents.

4. REAGENTS and MATERIALS

4.1 Acetic acid 0.5 N. Dilute 29.4 mL of concentrated acetic acid [American Chemical Society (ACS) reagent grade] to 1000 mL with reagent water.

4.2 Reagent water, Type IV in accordance with ASTM Specification D 1193 "Reagent Water". For organic parameters, the reagent water shall be free of any organic substances to be analyzed , Type I in accordance with ASTM Specification D 1193.

4.3 Nitric acid, 10% (v/v). Add 100 mL of concentrated nitric acid (ACS reagent grade) to 900 mL of reagent water.

4.4 Nitrogen gas, pre-purified, scrubbed through a molecular sieve.

5. SAMPLING

5.1 Collect a sufficient amount of sample to provide approximately 100 g of solid material, using techniques set out in US EPA SW-846 "Test Methods For Evaluating Solid Waste".

6. PREPARATION of APPARATUS

6.1 All glassware and equipment that comes into contact with the sample shall be cleaned in the following way before each use.

6.2 Wash with a non-phosphate detergent solution.

6.3 Rinse twice with tap water.

6.4 Rinse twice with reagent water.

6.5 Wash with 10% nitric acid.

6.6 Rinse several times with reagent water.

6.7 Store bottles filled with 10% nitric acid, until ready to use.

6.8 Rinse several times with reagent water before use.

6.9 Rinse clean oven dried bottles with methylene chloride, followed by methanol, for organic constituents.

7. PROCEDURES

7.1 Separation Procedure

7.1.1 If the sample contains a distinct liquid and a solid phase, separate it into its component phases using the following procedure.

7.1.2 Determine the dry mass of the solids in the sample at 60°C, using a well homogenised sample. Use this mass to determine the amount of material to be filtered.

7.1.3 Assemble the filtration unit with a filter bed consisting of a 0.45 µm pore size membrane filter and a coarse glass fibre pre-filter upstream of the membrane filter (per manufacturer's instructions).

7.1.4 Select one or more blank filters from each batch of filters. Filter 50 mL portions of reagent water through each test filter and analyze the filtrate for the analytical parameters of interest. Note the volume required to reduce the blank values to acceptable levels.

7.1.5 Wash each filter used in the leach procedure with at least this predetermined volume of water. Filter under pressure until no water flows through the filtrate outlet.

7.1.6 Remove the moist filter bed from the filtration unit and determine its mass to the nearest ± 0.01 g.

7.1.7 Re-assemble the filtration unit, replacing the filter bed, as before.

7.1.8 Grind the sample with a mortar and pestle, to a size that will pass through the opening of the filtration unit (less than 9.5 mm).

7.1.9 Agitate the sample by hand and pour a representative fraction of the solid and liquid phases into the opening of the filtration unit. Filter a sufficient amount of the sample to provide at least 60 g of dry solid material.

7.1.10 Pressurize the reservoir very slowly with nitrogen gas by means of the regulating valve on the nitrogen gas cylinder, until liquid begins to flow freely from the filtrate outlet.

7.1.11 Increase the pressure step-wise in increments of 50 kPa to a maximum of 500 kPa, as the flow diminishes. Continue filtration until the liquid flow ceases or the pressurizing gas begins to exit from the filtrate outlet of the filter unit.

7.1.12 De-pressurize the filtration unit slowly using the release valve on the filtration unit. Remove and weigh the solid material together with the filter bed to ± 0.01 g. Record the mass of the solid material.

7.1.13 Measure and record the volume and pH of the liquid phase. Store the liquid at 4°C under nitrogen until required in 7.2.13.

7.1.14 Discard the solid portion if the mass is less than 0.5% (w/v) of the fraction taken. If not, carry out the extraction procedure in 7.2

Note: For mixtures containing coarse grained solids, where separation can be performed without imposing a 500 kPa differential pressure, a vacuum filtration unit with a filter bed as described in 7.1.3 may be used. Vacuum filtration must not be used if volatile organic compounds are to be analysed.

7.2 **Extraction Procedure**

7.2.1 Prepare a solid sample for extraction by crushing, cutting or grinding, to pass through a 9.5 mm mesh sieve. If the original sample contains both liquid and solid phases, use the solid material from 7.1.14. The structural integrity

procedure in 7.3 should be used for monolithic wastes which are expected to maintain their structural integrity in a landfill, (e.g. some slags and treated solidified wastes).

Note: Do not allow the solid waste material to dry prior to the extraction procedure.

7.2.2 Determine the moisture content of the de-watered sample, by drying a suitable fraction to constant weight at 60°C in an oven. Discard the dried solid material.

7.2.3 Place the equivalent of 50 g dry mass of the de-watered undried material into a 1250 mL wide mouth cylindrical bottle. Use additional bottles, if a larger volume of leachate is required for the analysis.

7.2.4 Add 800 mL (less the moisture content of the sample in mL) of reagent water to the bottle.

7.2.5 Cap the bottle and agitate it in the rotary extractor for 15 minutes before measuring the pH.

7.2.6 Measure and record the pH of the solution in the bottle using a pH meter, calibrated with buffers at pH 7.00 and pH 4.00. The solution should be stirred during the pH measurement.

7.2.7 If the pH is less than 5.2, carry out the procedure comencing at 7.2.10.1.

7.2.8 Add a sufficient volume of 0.5N acetic acid if the pH is greater than 5.2 to bring the pH to 5.0 ± 0.2.

Note: Maximum Amount of Acid: No more than 4 mL of 0.5N acetic acid per gram of dry mass of sample may be added during the entire procedure. If the pH is not lowered to 5.0 ± 0.2 with this amount, proceed with the extraction.

7.2.9 Cap the bottle and place it in the solid waste rotary extractor. Rotate the bottle and its contents at 10 rpm for 24 hours at room temperature (20°C to 25°C).

7.2.10 Monitor, and manually adjust the pH during the course of the extraction, if it is greater than 5.2. The following procedure should be carefully followed:

7.2.10.1 Measure the pH of the solution after 1 hour, 3 hours and 6 hours from the starting time. If the pH is above 5.2, reduce it to pH 5.0 ± 0.2 by addition of 0.5N acetic acid. If the pH is below 5.0 ± 0.2, do not make any adjustments.

7.2.10.2 Adjust the volume of the solution to 1000 mL with reagent water, if the pH is below 4.8 after 6 hours.

7.2.10.3 Measure and reduce the pH to 5.0 ± 0.2, if required, after 22 hours and continue the extraction for an additional 2 hours.

7.2.11 Add enough reagent water at the and of the extraction period so that the total volume of liquid is 1000 mL. Record the amount of acid added and the final pH of the solution.

7.2.12 Separate the material into its component liquid and solid phases as described under the Separation Procedure (7.1). Discard the solid portion.

Note: It may be necessary to centifuge the suspension at high speed before filtration, for leachates containing very fine grained particles.

7.2.13 Calculate the amount of free liquid from 7.1.13 corresponding to 50 g of the dry solid material. Add this amount to the leachate from 7.2.12.

Note: If the analysis is not performed immediately, store separate fractions of the leachate at 4°C, after adding appropriate preservatives for the analytical parameters of interest (See "US EPA SW-846 "Test Methods For Evaluating Solid Waste".

7.2.14 Analyze the combined solutions from 7.2.13 using methods set ot in US EPA SW-846 "Test Methods For Evaluating Solid Waste"and which are capable of detecting the contaminants listed in Annex A, that are likely to be present at the detection limits specified for each contaminant.

7.2.15 Report concentrations of contaminants in the combined leachate and the free liquid solution as mg/L.

7.2.16 Carry a blank sample through the entire procedure, using dilute acetic acid at pH 5.0 ± 0.2.

7.3 **Structural Integrity Procedure**

7.3.1 This procedure may be required prior to extraction for some samples as indicated in 7.2.1. It may be omitted for wastes with known high structural integrity.

7.3.2 Fill the sample holder with the material to be tested. If the sample of the waste is a large monolithic block, cut a portion from the block measuring 33 mm in diameter by 71 mm in length. For a treated waste (e.g. solidified waste) samples may be cast in a form with the above dimensions for

the purposes of conducting this test. In such cases, the waste should be allowed to cure for 30 days prior to further testing.

7.3.3 Place the sample holder in the structural integrity tester, then raise the hammer to its maximum height and allow it to fall. Repeat this procedure 14 times.

7.3.4 Remove the material from the sample holder, and perform the extraction procedure (7.2). If the sample has not disintegrated, it may be sectioned; alternatively use the entire sample (after weighing) and a sufficiently large bottle as the extraction vessel. The volume of reagent water to be initially added is 16 mL/g of dry sample mass. The maximum amount of 0.5N acetic acid to be added is 4 mL/g of dry sample mass. The final volume of the leachate should be 20 mL/g of dry sample mass.

8. NOTES

8.1 ASTM publications are available from The American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

8.2 United States Government puublications are available from the Superintendant of Documens, US Government Printing Office, Washington DC 20402.

ANNEX A TO CGSB XX-GP-XXX

Contaminant	Concentration (mg/L)
2,4,5-TP / Silvex / 2-(2,4,5-Trichlorophenoxy) propionic acid	0.1
2,4-D	1.0
Aldrin + Dieldrin	0.007
Arsenic	0.5
Barium	10.0
Boron	50.0
Cadmium	0.05
Carbaryl / 1-Naphthyl-N-methyl carbamate / Sevin	0.7
Chlordane	0.07
Chromium	0.5
Cyanide	2.0
DDT	0.3
Diazinon / Phosphordithioic acid, o,o-diethyl o-(2-isopropyl-6-methyl-4-pyrimidinyl) ester	0.002
Endrin	0.002
Flouride	15.0
Heptachlor + Heptachlor epoxide	0.03
Lead	0.5
Lindane	0.04
Mercury	0.01
Methoxychlor / 1,1,1-Trichloro-2, 2-bis(p-methoxyphenyl) ethane	1.0
Methyl parathion	0.07

Contaminant	Concentration (mg/L)
Nitrate + Nitrite	100.0
Nitrilotriacetic acid	0.5
Nitrite	10.0
PCBs	0.03
Parathion	0.35
Selenium	0.1
Silver	0.5
Toxaphene	0.05
Trihalomethanes	3.5
Uranium	0.2

APPENDIX 6

ALBERTA LANDFILLING RULES

© 1994 NOVA HUSKY RESEARCH CORPORATION

PROVINCE OF ALBERTA

HAZARDOUS CHEMICALS ACT

HAZARDOUS WASTE REGULATION

Alberta Regulation 505/87

EXTRACT FROM THE
ALBERTA GAZETTE

Published by the Queen's Printer
for Alberta

Distributed by

Publication Services
11510 Kingsway Avenue
Edmonton T5G 2Y5
427-4952
FAX 451-4109

and

Publication Services
Main Floor, McDougall Centre
455 - 6th Street S W
Calgary T2P 4E8
297-6251

(Filed on December 18, 1987)

HAZARDOUS CHEMICALS ACT

(O.C. 824/87)

Approved and Ordered,
W. HELEN HUNLEY,
Lieutenant Governor, Edmonton, December 17, 19

Upon the recommendation of the Honourable the Minister of E Environment, the Lieutenant Governor in Council, pursuant to sect 16 of the Hazardous Chemicals Act, makes the regulation in t attached Appendix, being the Hazardous Waste Regulation.

DON R. GETTY (Chairm

A P P E N D I X

Hazardous Chemicals Act

HAZARDOUS WASTE REGULATION

Table of Contents

Definitions
Exemption 2--
Manifest form
Manifest completion
Generator's manifest duties
Copies accompanying waste
Carrier's manifest duties
Receiver's manifest duties
Retained copy
Multiple carriers' manifest
Storage facility
Storage
Bond
Unauthorized release report
Landfill disposal
Repeal
Coming into force

Schedule

Definitions

1 In this Regulation,

(a) "Act" means the *Hazardous Chemicals Act;*

(b) "carrier" means a person accepting for transportation or transporting hazardous wastes for storage, treatment or disposal;

(c) "container" means any portable device less than 454 litres in size in which a hazardous waste is stored;

(d) "empty container" means a container that contains less than 2.5 centimetres of residue remaining at the bottom of the container or less than 3% of the original contents, whichever is the lesser amount;

(e) "generator" means a person consigning hazardous wastes for storage, transportation, treatment, or disposal;

(f) "storage" means the holding of a hazardous waste for a temporary period at the end of which the hazardous waste is

(i) transported;

(ii) treated;

(iii) disposed of;

(g) "receiver" means a person receiving hazardous wastes for storage, treatment or disposal;

(h) "unrinsed empty container" means an empty container

(i) that has not been rinsed 3 times using for each rinse a clean solvent that is in an amount equal to 10% of the container volume and that is capable of removing the contained hazardous waste, or

(ii) that, in the opinion of the Director of Standards and Approvals of the Department, has not been rinsed by a method that produces results equal to or better than those produced by the method set out in subclause (i).

emption

The following hazardous chemicals are exempt from the Act and s Regulation if they are disposed of as waste:

(a) those wastes that are not listed in Table 1 of the Schedule or defined by the criteria specified in Table 1;

(b) household wastes;

(c) agricultural wastes generated by

(i) the growing and harvesting of agricultural crops, or

(ii) the raising of animals, including animal manures returned to the soil as fertilizers;

(d) mining overburden returned to a mine site as approved pursuant to the *Land Surface Conservation and Reclamation Act* and the regulations under that Act;

(e) fly ash waste, bottom ash waste, slag waste or flue gas emission control waste generated from the combustion of domestic waste, coal, or other fossil fuels as approved pursuant to the *Clean Air Act* or the *Clean Water Act* and the regulations under those Acts;

(f) drilling fluids, produced waters, oily waste, fracture fluids, reformates, completion fluids, process and run-off waters, spent iron sponge or similar sweeteners and waste treater hay resulting from the exploration, development or production of crude oil or natural gas approved pursuant to the *Oil and Gas Conservation Act* and the regulations under that Act, the *Oil Sands Conservation Act* and regulations under that Act or the *Pipeline Act* and regulations under that Act;

(g) irrigation return flows approved pursuant to the *Water Resources Act* and the regulations under that Act;

(h) domestic sewage;

(i) any materials that are for recycling, re-use or reprocessing in facilities approved pursuant to the *Clean Water Act* or the *Clean Air Act* and the regulations under those Acts;

(j) point source discharges licensed pursuant to the *Clean Water Act* or the *Clean Air Act* and the regulations under those Acts;

(k) agricultural chemicals and their empty containers approved pursuant to the *Agricultural Chemicals Act* and the regulations under that Act;

(l) any hazardous waste, except for those containing chemicals listed in Table 2 of the Schedule, produced by a generator in an amount less than 5 kilograms if a solid, or 5 litres if a liquid, per month.

Exemption

3 Section 7.4(1)(a), (b), (d) and (e) of the Act do not apply to a person who treats, stores or disposes of hazardous wastes generated by him on premises occupied by him.

Exemption

4 Sections 7.2, 7.3 and 7.4 of the Act do not apply to a hazardous waste which is transported not more than 1 km on a highway, as defined in the *Highway Traffic Act*, by or for a generator of the hazardous waste between the properties owned or leased by the generator if

(a) the local authority, as defined in the *Transportation of Dangerous Goods Control Act*, is informed of the movement and the nature of the hazardous waste, and

(b) the person in charge of the vehicle transporting the hazardous waste displays on the vehicle a placard that corresponds to the placard set out as Figure 19 in Part II of Schedule V of the *Transportation of Dangerous Goods Regulations* (SOR 85-77) under the *Transportation of Dangerous Goods Act* (Canada).

Manifest form

5 The manifest required by the Act shall be in the form set out in the *Transportation of Dangerous Goods Regulations* (SOR 85-77) under the *Transportation of Dangerous Goods Act* (Canada)..

Manifest completion

6 The applicable parts and copies of the manifest must be fully completed by the generator, carrier and receiver of hazardous wastes.

Generator's manifest duties

7 A generator shall

(a) on consigning a hazardous waste,

(i) certify the consignment on all copies of the manifest, and

(ii) have the carrier certify receipt of the waste,

(b) mail the 1st copy of the manifest to the Director of Pollution Control of the Department within 2 days, excluding Saturdays and holidays, after consigning the hazardous waste,

(c) retain the 2nd copy for at least 2 years following the consignment, and

(d) deliver the 3rd, 4th, 5th and 6th copies to the carrier.

Copies accompanying waste

8 The 3rd, 4th, 5th and 6th copies of the manifest must accompany the hazardous waste during transportation.

Carrier's manifest duties

9 The carrier shall

(a) on accepting a hazardous waste for transportation, certify the acceptance on all copies of the manifest,

(b) return the 1st and 2nd copies to the generator, and

(c) deliver the 3rd, 4th, 5th and 6th copies to the receiver.

Receiver's manifest duties

10 The receiver shall

(a) on accepting a hazardous waste for storage, treatment or disposal,

(i) certify the receipt on the 3rd, 4th, 5th and 6th copies of the manifest, and

(ii) return the 4th copy to the carrier,

(b) mail the 3rd copy to the Director of Pollution Control of the Department within 2 days, excluding Saturdays and holidays, after receiving the hazardous waste,

(c) retain the 5th copy for at least 2 years after receiving the hazardous waste, and

(d) mail the 6th copy to the generator within 2 days, excluding Saturdays and holidays, after receiving the hazardous waste.

Retained copy

11 The generator shall retain the 6th copy for at least 2 years following its receipt from the receiver.

Multiple carriers' manifest

12(1) If multiple carriers are used for 1 consignment of a hazardous waste,

(a) the generator shall fill out 1 manifest form with respect to each carrier,

(b) each carrier, on acceptance of the waste for transport, shall

(i) certify the receipt of the waste on 1 form and return copies 1 and 2 of that form to the generator, and

(ii) deliver the remaining manifest copies or remaining manifest forms or both to the receiver or next carrier,

and

(c) the receiver shall, on receiving the hazardous waste,

(i) certify the receipt of the waste on the 3rd, 4th, 5th and 6th copies of all manifest forms,

(ii) cross-reference all of the manifest,

(iii) mail the 3rd copy of each manifest form to the Director of Pollution Control of the Department within 2 days, excluding Saturdays and holidays, after receiving the waste,

(iv) mail the 4th copy of the appropriate manifest to each carrier,

(v) retain the 5th copy of each manifest for at least 2 years after receiving the waste, and

(vi) mail the 6th copy to the generator within 2 days, excluding Saturdays and holidays, after receiving the waste.

(2) A generator shall retain a copy for at least 2 years following its receipt from a receiver under subsection (1)(c).

Storage facility

13 A person who stores a hazardous waste shall, in a manner satisfactory to the Director of Standards and Approvals of the Department, store it so that

(a) any leakage is contained and prevented from entering into the remainder of the storage site and places beyond, including sewers and the ground underneath the site,

(b) the hazardous waste is adequately labelled, stating the identity of the contained waste, and

(c) the place where the hazardous waste is stored

(i) is secured from public entry,

(ii) is prominently identified as a hazardous waste storage site,

(iii) is equipped with suitable equipment to handle emergency situations, and

(iv) is provided with operators trained to respond to emergency situations specific to the substances stored.

Storage

14(1) No person shall store a hazardous waste that he did not produce unless he is a holder of a licence to operate issued under the *Clean Water Act* by the Director of Standards and Approvals of the Department.

(2) No person shall store a hazardous waste

(a) for a period exceeding 365 days, or

(b) in an amount exceeding 10 tonnes.

(3) Notwithstanding subsection (2), a hazardous waste may be stored for a period exceeding 365 days or in an amount exceeding 10 tonnes if the person who stores the hazardous waste is a holder of a licence to operate issued under the *Clean Water Act* by the Director of Standards and Approvals of the Department.

Bond

15 A person who operates a hazardous waste management facility shall provide to the Minister, if the Minister so requires, a bond in a form and in an amount that the Minister considers appropriate, and with an obligor and obligee acceptable to the Minister, to secure the performance of that person's obligations under the Act, the regulations, any agreement entered into with the Corporation and any conditions imposed by the Corporation respecting the storage, collection, transportation and treatment of hazardous wastes and the disposal of hazardous wastes and waste matter resulting from the treatment of hazardous wastes.

Unauthorized release report

16 Where an unlawful or accidental discharge, emission, escape or spill of a hazardous waste occurs at a facility for the storage, treatment or disposal of hazardous wastes, the person responsible for the hazardous waste shall, immediately on becoming aware of the occurrence, notify the Director of Pollution Control of the Department.

Landfill disposal

17(1) Hazardous wastes, except for those listed in subsection (3), may be disposed of in landfills that are approved for that purpose by the Director of Standards and Approvals of the Department.

(2) The Director of Standards and Approvals of the Department may approve the disposal of liquid hazardous wastes in a landfill that is provided with

(a) 2 liners of which at least 1 is a synthetic liner,

(b) a leachate collection and removal system,

(c) a leak detection system between the 2 liners, and

(d) a ground water monitoring system.

(3) Hazardous wastes that may not be disposed of into a landfill are

(a) liquid and solid hazardous wastes containing tri-, tetra-, and pentachlorophenol in a concentration greater than 1000 milligrams per kilogram;

(b) liquid or solid hazardous wastes containing any 1 or more of the following organic solvents in a concentration greater than 1000 milligrams per kilogram:

(i) acetone;

(ii) benzene;

(iii) n-butyl alcohol;

(iv) carbon disulfide;

(v) carbon tetrachloride;

(vi) chlorobenzene;

(vii) cresols and cresylic acid;

(viii) cyclohexanone;

(ix) ethyl acetate;

(x) ethyl benzene;

(xi) ethyl ether;

(xii) isobutanol;

(xiii) methanol;

(xiv) methylene chloride;

(xv) methyl ethyl ketone;

(xvi) methyl isobutyl ketone;

(xvii) nitrobenzene;

(xviii) 2-nitropropane;

(xix) pyridine;

(xx) tetrachloroethylene;

(xxi) toluene;

(xxii) 1,1,1 and 1,1,2-trichloroethane;

(xxiii) trichloroethylene;

(xxiv) xylene;

(c) liquid hazardous wastes containing free cyanides in excess of 1000 milligrams per kilogram;

(d) liquid hazardous wastes or earthen materials including, gravel, sand, clay and soil, that contain more than 50 parts per million by weight of polychlorinated biphenyls;

(e) hazardous wastes with a pH less than 2.0;

(f) liquid hazardous wastes containing the following contaminants in an amount equal to or greater than that shown:

(i)	arsenic	500 milligrams per kilogram;
(ii)	cadmium	100 milligrams per kilogram;
(iii)	chromium (Cr^{+6})	500 milligrams per kilogram;
(iv)	lead	500 milligrams per kilogram;
(v)	mercury	100 milligrams per kilogram;
(vi)	nickel	134 milligrams per kilogram;
(vii)	selenium	100 milligrams per kilogram;
(viii)	thallium	130 milligrams per kilogram.

Repeal

18 *The Hazardous Waste Regulation (Alta. Reg. 49/85) is repealed.*

Coming into force

19 *This Regulation comes into force on April 1, 1988.*

SCHEDULE

TABLE 1

1 Hazardous wastes listed in this Table consist of

(a) the goods, substances, and waste streams listed in List II of Schedule II in the English version of the *Transportation of Dangerous Goods Regulations* (SOR 85-77) under the *Transportation of Dangerous Goods Act* (Canada), except for those goods or substances which have the numeral "37" appearing in Column IV of that list;

(b) any container, other than an empty container, that is larger than 5 litres in capacity, and that was used to hold any goods, substances or waste streams referred to in clause (a), except for products or substances listed in Table 2;

(c) any unrinsed empty container larger than 5 litres in capacity that was used to hold any product or substance listed in Table 2.

2 Hazardous wastes defined by criteria in this Table are the following:

(a) any mixture or solution described by Classes 2 to 9 of section 3 in the English version of the *Transportation of Dangerous Goods Regulation* (SOR 85-77) made under the *Transportation of Dangerous Goods Act* (Canada), or

(b) any mixture or solution which contains 0.01 percent by mass or greater of any of the substances listed in section 1(a) with the numerals "9.2" appearing in Column III of the list referred to in section 1(a).

TABLE 2

CHEMICALS THAT MAKE UNRINSED EMPTY CONTAINERS HAZARDOUS WASTE

Substance
Acetaldehyde, chloro-
Acetamide, N-(aminothioxomethyl)-
Acetamide 2 fluoro
Acetic acid fluoro sodium salt
[illegible]
3-(alpha-Acetonylbenzyl)-4-hydroxycoumarin and salts, when present at concentrations greater than 0.3%
1-Acetyl 2 thiourea
Acrolein
Aldicarb
Aldrin
Allyl alcohol
Aluminum phosphide
5-(Aminomethyl)-3-isoxazolol
4 Aminopyridine
Ammonium picrate
Ammonium vanadate
Arsenic acid
Arsenic (III) oxide
Arsenic (V) oxide
Arsenic pentoxide
Arsenic trioxide
Arsine, diethyl-
Aziridine
Barium cyanide
Benzenamine, 4-chloro-
Benzenamine, 4-nitro-
Benzene, (Chloromethyl)
1,3 Benzenediol, 4-[1-hydroxy-2-(methylamino)ethyl]
Benzenethiol
Benzyl chloride
Beryllium dust
Bis(chloromethyl) ether
Bromoacetone
Brucine
Calcium cyanide
Camphene, octachloro-
Carbamimidoselenoic acid
Carbon bisulfide
Carbon disulfide
Carbonyl chloride
Chlorine cyanide
Chloroacetaldehyde
p-Chloroaniline
1 (o Chlorophenyl)thiourea
3 Chloropropionitrile
Copper cyanides
Cyanides (soluble cyanide salts), not elsewhere specified
Cyanogen
Cyanogen chloride
Dichlorophenylarsine
Dieldrin
Diethylarsine
0,0-Diethyl S [2 (ethylthio)ethyl] [illegible]

Substance
Diethyl-p-nitrophenyl phosphate
0,0 Diethyl O-pyrazinyl phosphorothioate
Diisopropyl fluorophosphate
[illegible]
[illegible] butanone, O-[(methylamino)carbonyl] oxime
0,0-Dimethyl O p-nitrophenyl phosphorothioate
Dimethylnitrosamine
alpha, alpha-Dimethylphenethylamine
4,6-Dinitro-o-cresol and salts
4,6-Dinitro-o-cyclohexylphenol
2,4-Dinitrophenol
Dinoseb
Diphosphoramide, octamethyl-
Disulfoton
2,4-Dithiobiurel
Dithiopyrophosphoric acid, tetraethyl ester
Endosulfan
Endothall
Endrin
Epinephrine
Ethenamine, 1,1-dimethyl-2-phenyl
Ethenamine, N-methyl-N-nitroso-
Ethyl cyanide
Ethylenimine
Famphur
Fluorine
Fluoroacetamide
Fluoroacetic acid, sodium salt
Fulminic acid, mercury (II) salt
Heptachlor
1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo, endo- 1,4:5,8-dimethanonaphthalene
1,2,3,4,10,10 Hexachloro 6,7 epoxy 1,4,4a,5,6,7,8,8a octahydro endo, exo- 1,4:5,8 dimethanonaphthalene
1,2,3,4,10,10-Hexachloro- 1,4,4a,5,8,8a-hexahydro- 1,4:5,8-endo, endo-dimethanonaphthalene
1,2,3,4,10,10-Hexachloro- 1,4,4a,5,8,8a-hexahydro- 1,4:5,8-endo, exo-dimethanonaphthalene
Hexachlorohexahydro-exo, exo-dimethanonaphthalene
Hexaethyl tetraphosphate
Hydrazinecarbothioamide
Hydrazine, methyl-
Hydrocyanic acid
Hydrogen cyanide
Hydrogen phosphide
Isocyanic acid, methyl ester
3(2H)-Isoxazolone, 5-(aminomethyl)
Mercury, (acetato-O)phenyl
Mercury fulminate
[illegible]

TABLE 2 (cont'd)

CHEMICALS THAT MAKE UNRINSED EMPTY CONTAINERS HAZARDOUS WASTE

Substance
Methane, tetranitro-
Methanethiol, trichloro-
4,7 Methano 1H indene, 1,4,5,6,7,8,8 [illegible] hydro-
Methomyl
2-Methylaziridine
Methyl hydrazine
Methyl isocyanate
2-Methyllactonitrile
Methyl parathion
alpha-Naphthylthiourea
Nickel carbonyl
Nickel cyanide
Nickel (II) cyanide
Nickel tetracarbonyl
Nicotine and salts
Nitric Oxide
p-Nitroaniline
Nitrogen dioxide
Nitrogen (II) oxide
Nitrogen (IV) oxide
Nitroglycerine
N-Nitrosodimethylamine
N-Nitrosomethylvinylamine
5-Norbornene-2,3-dimethanol), 1,4,5,6,7,7-hexachloro, cyclic sulfite
Octamethylpyrophosphoramide
Osmium oxide
Osmium tetroxide
7-Oxabicyclo [2.2.1] heptane-2,3-dicarboxylic acid
Parathion
Phenol, 2-cyclohexyl-4,6-dinitro
Phenol, 2,4-dinitro-
Phenol, 2,4-dinitro-6-methyl-
Phenol, 2,4 dinitro-6-(1-methylpropyl)-
Phenol, 2,4,6-trinitro, ammonium salt
Phenyl dichloroarsine
Phenylmercuric acetate
N-Phenylthiourea
Phorate
Phosgene
Phosphine
Phosphoric acid, diethyl p-nitrophenyl ester
Phosphorodithioic acid, 0,0-dimethyl S [2 (methylamino) 2-oxoethyl] ester
Phosphorofluoric acid, bis(1 methylethyl)-ester
Phosphorothioic acid, 0,0-diethyl S [(ethylthio)methyl] ester
Phosphorothioic acid, 0,0 diethyl O (p-nitrophenyl) ester
Phosphorothioic acid, 0,0-diethyl O-Py[illegible] es[illegible]

Substance
Phosphorothioic acid, 0,0 dimethyl-O-[p-((dimethylamino-sulfonyl) phenyl] ester
Phosphorus, [illegible]
Potassium cyanide
Potassium silver cyanide
Propanal, 2-methyl-2-(methylthio)-, O[(methylamino)Carbonyl]oxime
Propanenitrile
Propanenitrile, 3-chloro-
Propanenitrile, 2 hydroxy-2-methyl-
1,2,3-Propanetriol, trinitrate-
2-Propanone, 1-bromo-
Propargyl alcohol
2-Propenal
2 Propen 1-ol
1,2 Propylenimine
2-Propyn-1-ol
4-Pyridinamine
Pyridine, (S)-3-(1-methyl-2-Pyrrolidinyl)-, and salts
Pyrophosphoric acid, tetraethyl ester
Selenourea
Silver cyanide
Sodium azide
Sodium cyanide
Strontium sulfide
Strychnidin-10 one, and salts
Strychnidin-10-one, 2,3,-dimethoxy-
Strychnine and salts
Sulfuric acid, thallium(I) salt
Tetraethyldithiopyrophosphate
Tetraethyl lead
Tetraethylpyrophosphate
Tetranitromethane
Tetraphosphoric acid, hexaethyl ester
Thallic oxide
Thallium (III) oxide
Thallium (I) selenite
Thallium (I) sulfate
Thiofanox
Thioimidodicarbonic diamide
Thiophenol
Thiosemicarbazide
Thiourea (2-chlorophenyl)-
Thiourea, 1 naphthalenyl-
Thiourea, phenyl-
Toxaphene
Trichloromethanethiol
Vanadic acid, ammonium salt
Vanadium pentoxide
Vanadium (V) oxide
Warfarin, when present at concentrations greater than 0.3%
Zinc cyanide
Zinc Phosphide, when present at concentrations greater than 10%

APPENDIX 7

TRANSPORT OF DANGEROUS GOODS ACT
SEC. 3.19

FORMULA FOR TOXICITY DETERMINATION

© 1991 NOVA HUSKY RESEARCH CORPORATION

Determination of LD_{50} value or LC_{50} value of a poisonous mixture.

Determination of LC_{50} and LD_{50} values for poisonous mixtures or solutions.

3.23 (1) For the purposes of Sections 3.19 and 3.21 where the LD_{50} value of a product is unknown

Sect. 3.19: Criteria for Class 6.1 Sect. 3.21: Packing groups in Class 6

(a) and the product is a mixture or solution containing only one poisonous substance, the LD_{50} value of the product may be calculated using the following formula;

$$\text{LD}_{50}\text{ value of the product} = \frac{\text{LD}_{50}\text{ of poisonous substance} \times 100}{\text{percentage of poisonous substance by mass}}$$

(b) and the product is a mixture of solution containing more than one poisonous substance,

(i) the LD_{50} of each poisonous substance in the product may be calculated according to paragraph (a), and

(ii) where the LD_{50} value of each substance is calculated pursuant to paragraph (a), the LD_{50} value of the total mixture may be calculated using the following formula, namely,

[S8:17 18/1/89]

$$\frac{1}{\text{LD}_{50}\text{ of mixture}} = \frac{1}{\text{LD}_{50}\text{ of 1st substance}} + \frac{1}{\text{LD}_{50}\text{ of 2nd substance}} + \ldots + \frac{1}{\text{LD}_{50}\text{ of last substance}}$$

(2) For the purposes of sections 3.11, 3.19 and 3.21, where the LC_{50} value of a product is unknown

[S3:31 27/6/85]
Sect. 3.11: Criteria for Classes 2.3, 2.4. Sect. 3.19: Criteria for Class 6.1 Sect. 3.21: Packing groups for Class 6.

(a) and the product is a mixture or solution containing only one poisonous substance, the LC_{50} value of the product may be calculated using the following formula:

$$\text{LC}_{50}\text{ value of the product} = \frac{\text{LC}_{50}\text{ of poisonous substance} \times 100}{\text{percentage of poisonous substance by mass}}$$

(b) and the product is a mixture or solution containing more than one poisonous substance,

(i) the LC_{50} of each poisonous substance in the product may be calculated according to paragraph (a), and

(ii) where the LC_{50} value of each substance is calculated pursuant to paragraph (a), the LC_{50} value of the total mixture may be calculated using the following formula, namely, [S8:17 18/1/89]

$$\frac{1}{LC_{50} \text{ of mixture}} = \frac{1}{LC_{50} \text{ of 1st substance}} + \frac{1}{LC_{50} \text{ of 2nd substance}} + \ldots + \frac{1}{LC_{50} \text{ of last substance}}$$

(3) The formulae set out in subsections (1) and (2) shall not be used for mixtures containing both LC_{50} and LD_{50} at the same time.

Class 7 - Radioactive materials

Definition of Class 7.

3.24 Products, substances or articles containing a product or substance with activity greater than 74 kBq/kg are radioactive materials and included in Class 7 referred to in the schedule to the Act.

Class 8 - Corrosives

Criteria for Class 8.

3.25 (1) Not fully specified products or substances that

(a) have been known to cause visible necrosis of human skin tissue,

(b) cause visible necrosis of the skin tissue of an albino rabbit at the contact site within a period of four hours or less when administered by continuous contact with the intact bare skin of the rabbit,

(c) corrode SAE 1020 steel or 7075-T6 non-clad aluminum surfaces at a rate exceeding 6.25 mm per year at a test temperature of 55° C using the metal corrosion test method set out in Part VI of Schedule VI, or

Schedule VI: Test Methods 6.25 mm = 0.25 inch. 55° C = 131° F

(d) are wastes that have a pH factor less than 2.0 or greater than 12.5

shall be included in Class 8 referred to in the schedule to the Act.

(2) For the purposes of subsection (1), not fully specified products or substances that are wastes include [S12:4 1/6/89]

(a) wastes that are solids that, when prepared in a 50 per cent by mass mixture or solution with distilled water, meet the criteria set out in subsection (1); and

(b) wastes that are liquids.

Amended June, 1989

APPENDIX 8

MICROTEX EC50 VALUES OF METAL IONS

© 1991 NOVA HUSKY RESEARCH CORPORATION

MICROTOX EC50 VALUES OF METAL IONS		
METAL ION	**CHEMICAL**	**EC50 (15min)***
Al^{+3}	$Al_2(SO_4)_3.18H_2O$	1.1
As^{+3}	$NaAsO_2$	26
Cd^{+2}	$CdCl_2$	20
Co^{+2}	$CoCl_2.6H_2O$	5
Cr^{+3}	$KCr(SO_4).12H_2O$	15.3
Cr^{+6}	$K_2Cr_2O_7$	18
Cu^{+2}	$CuCl_2.2H_2O$	0.8
Fe^{+3}	$Fecl_3.6H_2O$	0.8
Hg^{+2}	$HgCl_2$	**
Mn^{+2}	$Mn(NO_3)_2$	13.7
Ni^{+2}	$NiCl_2.6H_2O$	100
Pb^{+2}	$Pb(NO_2)_2$	0.6
Se	Se	
Se^{+4}	Na_2SeO_2	33
Zn^{+2}	$ZnSO_4.7H_2O$	4

* Expressed as the metal ions in 1 mg per liter or ppm.

** Not reported.

Obtained from MICROBICS Corporation, Carlsbad, CA.

© 1991 NOVA HUSKY RESEARCH CORPORATION